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VOLUME 9 Nos. 5/6

JUNE 1956

PERGAMON PRESS · LONDON & NEW YORK

Geochim. et Cosmochim. Acta

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Publishing Offices: Pergamon Press Ltd., 4 & 5 Fitzroy Square, London W.1. (EUS 4455)

Subscription per volume (including postage) (A) £5 10s. (U.S.A. $15.40); (B) For individual subscribers certifying that the journal is for their private use, £3 10s. (U.S.A. $9.80)

Back numbers, £7 ($19.60) per volume)

Distributors: I. R. Maxwell & Co., Ltd., 4 & 5 Fitzroy Square, London W.1

and Pergamon Press, Inc., 122 East 55th Street, New York 22, N.Y.

PERGAMON PRESS LTD., 4 & 5 FITZROY SQUARE, LONDON W.1
PERGAMON PRESS, INC., 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Geochimica et Cosmochimica Acta, 1956, Vol. 9, pp. 217 to 248. Pergamon Press Ltd., London

A chemical definition of fractionation stages as a basis for comparison of Hawaiian, Hebridean, and other basic lavas

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(*Received* 24 *June* 1955)

ABSTRACT

Accepting that crystal fractionation of basic magma leads to simultaneous increases in the iron ratios $\left(\frac{Fe\cdot\cdot + Mn}{Fe\cdot\cdot + Mn + Mg}\right)$ and the albite ratios $\left(\frac{\text{normative molecular albite}}{\text{normative molecular albite} + \text{anorthite}}\right)$, a graphical plotting of these two ratios, one against the other, provides a method of defining successive stages of fractionation. By averaging the analyses falling in the different fractionation stages for the two main types of basalt, the Plateau and Tholeiitic, a better chemical definition of these is obtained, and of the composition of the Alkaline and Tholeiitic magma series to which they give rise.

Preliminary averaging of analyses of basalts from other regions indicates that at comparable stages, some are relatively rich in SiO_2 and can be grouped as tholeiitic basalts, and others are poor in SiO_2 and have alkaline basalt characteristics, while yet others have intermediate chemical features. Comparison of averages for different fractionation stages also shows minor chemical differences which are believed characteristic of particular regions.

Vast numbers of basalts have now been described in varying detail, and many chemical data have been obtained. From the field relations and investigations of mineral composition and order of crystallization, combined with chemical analyses, various attempts are made from time to time to decide first, on a natural grouping of the basalts into types, and then, on the average chemical composition of the types. It will be a long time before there are enough chemical data to allow a purely statistical handling of them to be used in defining the dominant types. At present a method of trial and error is necessary; an attempt is made to grasp the actual variation occurring, then as far as possible to understand the reason for it, so that the characteristics to be regarded as significant for a sound classification of basalts may be decided. The data are then re-examined, and it is hoped that a nearer approach to a natural classification is reached. In the present paper an attempt is made to use an additional method, implicit in other treatments but not previously clearly distinguished. This is to evaluate the effect of fractional crystallization—the results of which process upon basic magma are now becoming more fully understood—and then to disentangle the effects of this factor from the variations due to differences in the parent magma.

Plotting Basalt Analyses to Sort Out Successive Stages of Fractionation

Various different methods of graphically plotting analyses of rocks have been successfully used for specific purposes. One of the oldest methods is to plot the amounts of elements or oxides against the silica percentage of the rock. This type of plot, known generally as a silica variation diagram, may be used to indicate chemical relationship between rocks of a single magmatic province and to compare different provinces. Larsen (1938), followed by others, has plotted against a more complex factor involving other elements, but still largely dominated by the

amount of silica; it is remarkable how smooth the variation in chemical composition of rocks of a single province often proves to be when plotted in this way (cf. Nockolds and Allen, 1953, 1954).

It is often assumed, when plotting against silica percentage, or Larsen's more complex factor, that the sequence of rocks showing increasing silica content is in fact a succession due to differentiation by fractional crystallization. This is an assumption which is only valid if it so happens that increasing silica percentage accompanies crystal fractionation, which is probably often, but not always, the case.

The primary object of the present paper is to use plots of analyses, not to show chemical variation within a group of rocks, but to indicate the probable sequence in which the rocks were produced if they resulted from crystal fractionation. With this objective there is an advantage in using certain ratios rather than absolute amounts. A preliminary attempt to use ratios of iron to magnesium on the one hand and albite to anorthite on the other was made in the paper on the Skaergaard Intrusion (Wager and Deer, 1939, p. 310 and Fig. 58). Poldervaart and Elston (1954) have used the iron-to-magnesium ratio and plotted this against what they describe as the linkage factor, which is related to SiO_2 content of the rock. In rather the same way Simpson (1954) has plotted an iron-to-magnesium ratio against what he described as a felsic index, a ratio involving alkalis and lime. In plotting the results of chemical analyses in these ways, the aim is primarily to show the differentiation sequence. It is believed that certain ratios are of especial value when the differentiation sequence is being established, while plots of the actual amounts of the elements are necessary when the general chemical variation of a suite of rocks is being illustrated.

Crystal fractionation of basic magma is dominantly controlled in the early stages by the separation of olivine, pyroxenes, and basic plagioclase. Because the early, high-temperature ferro-magnesian minerals are richer in magnesium than the later, lower-temperature solid solutions, there is an increasing proportion of iron relative to magnesium in the successive crystal fractions and also in the corresponding residual liquids. Similarly, because the early plagioclase is richer in anorthite, there is an increasing proportion of albite relative to anorthite in the successive crystal and liquid fractions. When iron ores separate, usually as titaniferous magnetite, there is a slowing up of the rate of increase of iron relative to magnesium in the residual liquid; this is probably not usually enough to mask the general increase in the iron-to-magnesium ratio. These generalizations are satisfactorily based on observations of naturally occurring cases of fractionation of basic magma, and on experimental investigations of systems involving olivine, pyroxene, and plagioclase. Although there is a difference of opinion about the extent of total iron enrichment during fractionation, there is none about the increase in iron relative to magnesium, nor about the increase of albite relative to anorthite. The iron-to-magnesium and the albite-to-anorthite ratios are thus considered the best criteria for deciding the degree of fractionation which has taken place among basic rocks.

Silica does not crystallize as a separate mineral in the early stages of solidification of basic magma, but, as a result of several different factors, it is usually

more abundant in relation to the other main constituents in the successive later liquid fractions. Thus increasing silica percentage, and such functions as LARSEN's which is dominated by SiO_2 percentage, may often define the line of liquid descent as mentioned earlier (p. 217), although it is not regarded as so reliable a criterion as the iron-to-magnesium and albite-to-anorthite ratios.

The iron-to-magnesium ratio and the albite-to-anorthite ratio, calculated from the analyses, may be conveniently plotted one against the other as is done for the analyses of Hawaiian and Hebridean basalts and related lavas in Figs. 2 and 5. The particular iron-to-magnesium ratio used is $\frac{Fe^{\cdot\cdot} + Mn^{\cdot\cdot}}{Mg + Fe^{\cdot\cdot} + Mn}$ in terms of the number of atoms, and in what follows this is called briefly the iron ratio. An iron-to-magnesium ratio in which both ferrous and ferric iron are included, namely $\frac{Fe^{\cdot\cdot\cdot} + Fe^{\cdot\cdot} + Mn^{\cdot\cdot}}{Mg^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} + Fe^{\cdot\cdot} + Mn^{\cdot}}$, has been used by various authors, e.g., NIGGLI's mg value (cf. NIGGLI and PARKES, 1954). It is not used here, because ferric iron does not replace Mg diadochically and therefore introduces new and not well-understood factors. Furthermore, increasing ferric iron in successive liquid fractions is not likely to be important when iron ore is one of the phases being precipitated, and this occurs at about the middle stage of crystallization of basic magma. The trend of composition of successive liquid fractions is no doubt considerably affected by the degree of oxidation of the crystallizing basic magma, and this can be appreciated if ferric iron is not included with the ferrous. If, however, oxidation of some of the iron took place after fractionation, i.e., during or after the cooling down of the rock, then, by excluding the ferric iron from the iron-to-magnesium ratio, an incorrect assessment of the stage of crystal fractionation will be obtained. Satisfactory iron ratios are not always available, because the proportion of $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ in many of the older analyses was not adequately determined. In plotting the Hawaiian basalts, some early analyses have had to be excluded because of this, or because the high $Fe^{\cdot\cdot\cdot}$ suggests oxidation of the rock at some stage subsequent to differentiation.

The albite-to-anorthite ratio used here, called for simplicity the albite ratio, is the normative molecular ratio Ab/Ab + An. If nepheline occurs in the norm, it has been converted to albite and added to the amount of normative Ab before obtaining the ratio, a procedure considered satisfactory for the more ordinary basalts with which this paper is concerned, since nepheline is not found as a crystal phase in these rocks.

Bearing in mind the significance of the iron and albite ratios, it is clear that basalts of an early stage in the fractionation process are those with low albite and iron values, while basalts of later stages of fractionation have increasingly higher values. It may also be noted here that the basalts with lower iron and albite ratios would require a higher temperature to make them completely liquid. The meaning to be attached to the term 'fractionation stage' requires, however, to be made more precise. Thus it is best defined chemically from the composition of successive liquids, and not from the composition of the precipitate of crystals formed from these liquids. This may be illustrated by consideration of the Skaergaard Intrusion. A plot for successive rocks and corresponding liquids of the

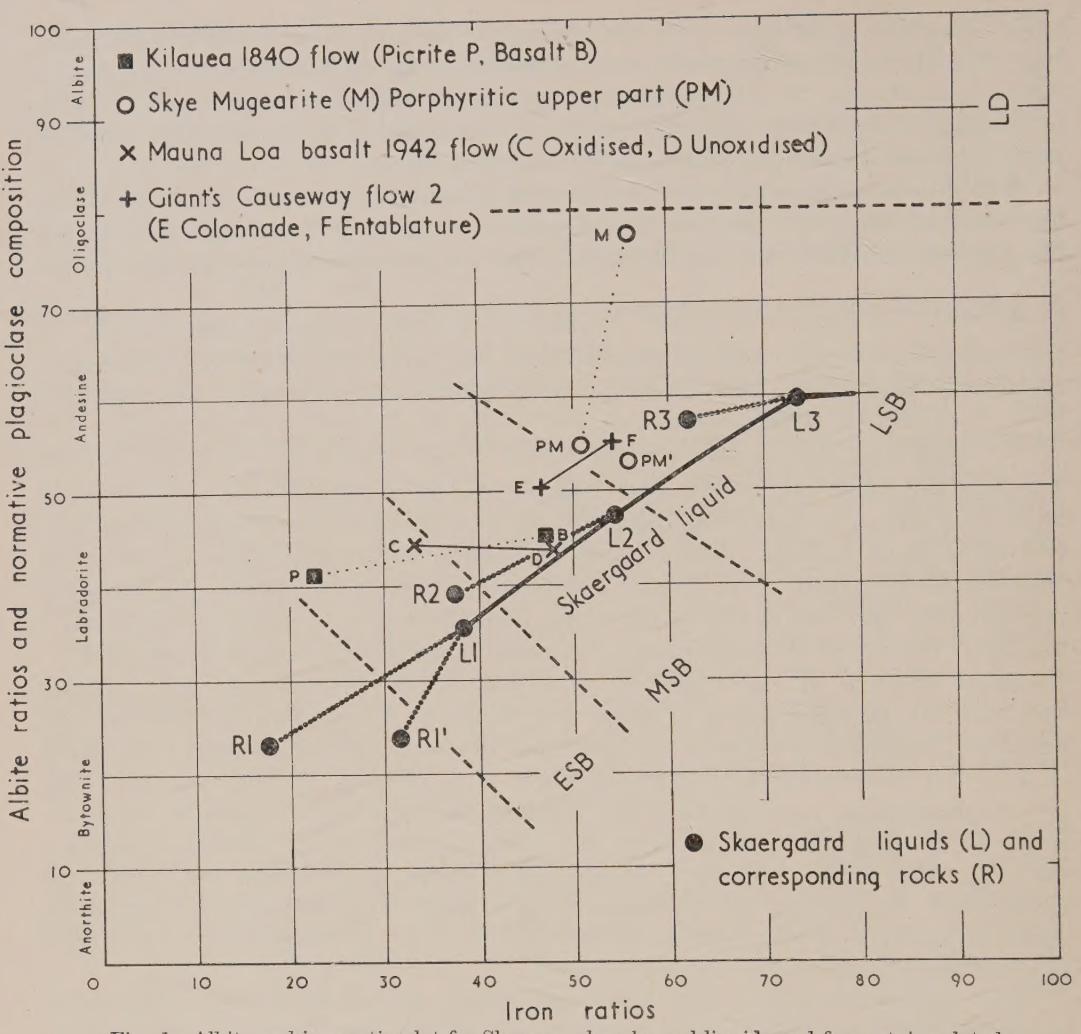


Fig. 1. Albite and iron ratio plot for Skaergaard rocks and liquids and for certain related pairs of basalts.

L1, original Skaergaard liquid; L2 and L3, later residual liquids. R1, gabbro picrite (1682) and R1′, Perpendicular Felspar rock (1851) corresponding to liquid L1; R2, hypersthene olivine gabbro (4077) corresponding to liquid L2; R3, ferrogabbro (1907) corresponding to liquid L3.

P, B. Basalt flow of 1840 (Macdonald, 1949b, p. 1572). B basalt from an upper vent. P Picrite basalt from a lower vent.

M, PM. Mugearite and Porphyritic Mugearite from composite flow, Skye. PM[1] represents calculated position of mugearite with 50 per cent labradorite added.

C, D. Oxidized and unoxidized Mauna Loa basalt from a single flow (Macdonald, 1949b, p. 1572). The unoxidized, D, was extruded a little later than the oxidized, C.

E, F. Giant's Causeway, flow 2 (E, colonnade; F, entablature).

Skaergaard Intrusion (Fig. 1) shows the original Skaergaard liquid (L1), the arbitrary second liquid when about 60 per cent had crystallized (L2), and an arbitrary third liquid when about 88 per cent had crystallized (L3). Estimates of the composition of later liquids are not wholly satisfactory and are not plotted. The graph shows how the later liquid fractions have higher iron and albite ratios.

Rocks which represent the crystal fractions with only 20 or 30 per cent of material derived from the interprecipitate liquid are also plotted for the various stages. Thus the hypersthene-olivine gabbro R2 was formed from the liquid L2, and the ferrogabbro R3 from the liquid L3. As would be anticipated, the rocks, which consist largely of primary precipitate crystals, are lower in albite and iron ratios than the corresponding liquid, because 70–80 per cent of the rock is made up of more anorthite-rich plagioclase and more magnesium-rich pyroxene and olivine than the average of these minerals which would be obtained on total crystallization of the liquid at that stage. For a layered intrusion such as the Skaergaard, the stage of fractionation might be defined by the composition of either the crystal fraction or the liquid from which the crystals formed, but not both, as the liquid and the simultaneously precipitated rock have different ratios.

In dealing with non-porphyritic lavas, we may be sure that we have a close approach to the composition of a liquid phase, which, to use BOWEN's useful phrase, lies on the line of liquid descent; but when phenocrysts are present, there are two possibilities, not usually distinguishable. The phenocrysts may be the result of intratelluric crystallization of the magma without relative movement of crystals and liquid, and in this case the composition of the rock, including its phenocrysts, will still be on the line of liquid descent. On the other hand, the phenocrysts may have resulted from crystal accumulation, in which case the analyses of the rocks do not lie on the line of liquid descent, but are related to it as the accumulative rocks of the Skaergaard layered series are related to the corresponding liquids. An interesting example among volcanic rocks is the case described by MACDONALD (1943 and 1949b; p. 1572, Anal. 1 and 2) from Mauna Loa. Aphyric basalts from an upper vent were extruded simultaneously with olivine-phyric picrite basalt from a lower vent, and the contrast is explained by MACDONALD as the result of the accumulation of olivine crystals by gravity in the lower part of the magma column supplying the vents. The analyses of the two lava types have been plotted (Fig. 1) and, as might be expected, the albite ratio shows little variation, since increase or decrease in the amount of olivine phenocrysts would not affect this. On the other hand, the iron ratio is lower in the rock with an accumulation of early olivine crystals, because these olivines are poorer in iron than the average of those which would crystallize from the original undifferentiated magma.

Analyses of all types of Hawaiian lavas given by MACDONALD (1949a, b), excluding only those with unsatisfactory ferric iron values, are shown in the albite and iron ratio plot (Fig. 2). The picrite basalts lie in a well-defined situation on the left-hand side of the general trend of the points. MACDONALD (1949a, b), POWERS (1955), and also earlier workers, have given good reasons for accepting the view that the picrite basalts are ordinary basalts enriched by the addition from an overlying part of the liquid of early olivine, usually Fa_{20-30}. In the same part of the graph as the picrite basalts are a few olivine basalts, but it is noteworthy that many of the olivine basalts are on the general trend line, and in these cases it may be that the phenocrystic olivine is not the result of accumulation, but represents early intratelluric crystallization of this mineral.

In the Hebridean province, the Porphyritic Central basalts of the authors of

the Mull Memoir are rich in plagioclase, some being perhaps due to the addition of early plagioclase crystals to more ordinary magma. This should affect the albite, but not the iron ratio, and it should result in a downward shift of the points from the position of the corresponding basalt free from porphyritic plagioclase, because

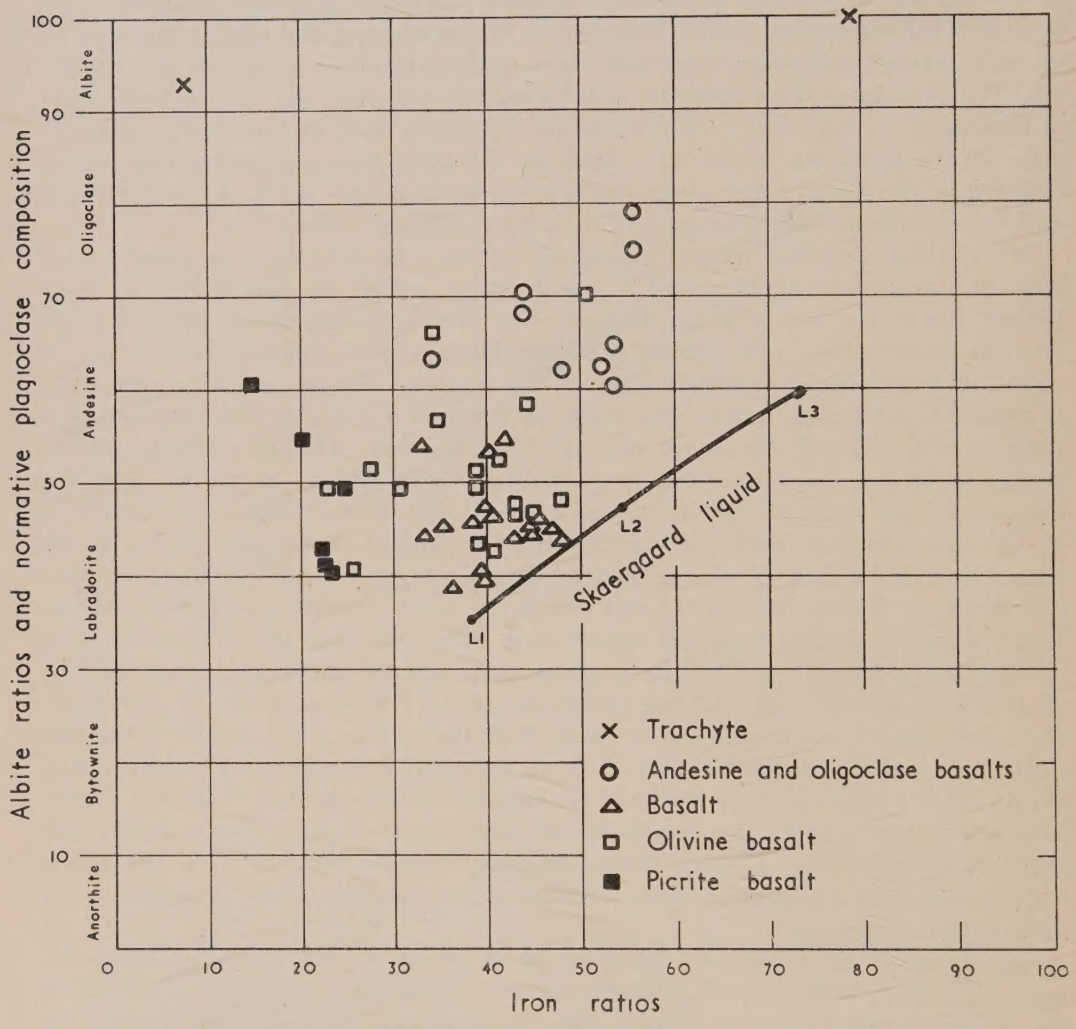


Fig. 2. Albite and iron ratio plot of Hawaiian lavas divided into types, following Macdonald.

the added plagioclase would be richer in anorthite than the average. The points for a composite mugearite flow from Skye (Harker, 1904, p. 263; cf. also Kennedy, 1931) illustrate this kind of effect (Fig. 1); point M is the composition of the lower non-porphyritic part of the flow; point PM the position of the upper unit with abundant phenocrysts of labradorite, and point PM′ is the position of the calculated mixture (Kennedy, 1931, p. 177), consisting of the non-porphyritic mugearite M with the addition of 50 per cent of labradorite.

While discussing the effects on the plotted positions of the addition of crystals to the magma, it is also convenient to consider in general terms the effect of oxidation of basic magma mentioned briefly on page 219. Oxidation of Fe· · to Fe · · · will reduce the iron ratio, since the amount of ferrous iron is diminished by conversion of some to ferric. Oxidation will therefore move the plotted point leftwards from the position of the unoxidized material. MACDONALD (1949b, p. 1572, Anal. 4 and 5) gives two analyses of lava from the same eruption. They are very similar except that the earlier is markedly more oxidized. The plot of the more oxidized (Fig. 1 C) is to the left of the less oxidized (D). The trend line for the particularly reduced Skaergaard liquids lies to the right of the points for the usually more-oxidized Hawaiian lavas (Fig. 2).

When porphyritic lavas, or plutonic rocks which may not have the composition of a liquid, are being considered, the stage of fractionation cannot with certainty be defined by the method of plotting used here. If there is an indication from the abundance of porphyritic crystals that the lava analysed is partly the result of crystal accumulation, then the direction of shift of the plotted point, which would make it more closely correspond with the presumed composition of the magma, may be shown in the plots by an arrow; see, for example, the Hawaiian Alkaline magma series (Fig. 3). In the same way, if the analysis suggests an oxidized material, a line may be attached to the point indicating the direction of shift towards the presumed unoxidized magma (Fig. 3). In both cases there is no certainty that the liquid had a different composition from the rock analysed, and the symbols indicate only the likely shift of position.

Composition at Successive Fractionation Stages of Hawaiian Basalts of the Alkaline and Tholeiitic Series

The spread of points for the Hawaiian lavas and successive Skaergaard intrusion liquids (Figs. 3 and 4) has been divided by lines crossing the general trend in order to define fields of what are arbitrarily named primary, early, middle, and late stage basalts and late differentiates.* These broad fields have in some cases been split again into α and β divisions, but this often is an over-refined classification. The basalts falling within each of the fields are considered to be at approximately the same stage of fractional crystallization, although points for analyses of rocks affected strongly by crystal accumulation or magma oxidation may be anomalous. The plotting does not distinguish different magma types; provided they are at approximately the same stage of fractionation, they will be brought together on the graph. Field and petrographic studies, or other methods of considering the chemical analyses, have to be used to decide whether the basalts of any one stage belong to significantly different types.

MACDONALD (1949a, b), POWERS (1955), and also earlier authors, have shown

* Although described here in terms of fractionation stages, some of the basaltic rocks may not have been produced by fractionation, but have resulted from fusion or partial fusion of pre-existing material. However, whether produced in one way or the other, the basalt material of the different stages will differ in the temperature required to make it completely liquid, the early-stage basalt being the higher temperature, and the late-stage, the lower. It would have been, in many ways, more satisfactory to have used the terms high-, middle-, and low-temperature basalts, but this terminology has been avoided for the present as being a less direct deduction from the data.

that there is a relationship between the types of lava in Hawaii and the present stage of development of the volcanoes from which they come. In particular there is a so-called primitive stage in the development of the volcanoes typified by Mauna Loa and Kilauea, where the lavas vary within narrow limits, and are described as primitive olivine basalt or primitive picrite basalt. The other volcanoes—Hualalai, Mauna Kea, and Kohala—are in, or have passed through, a

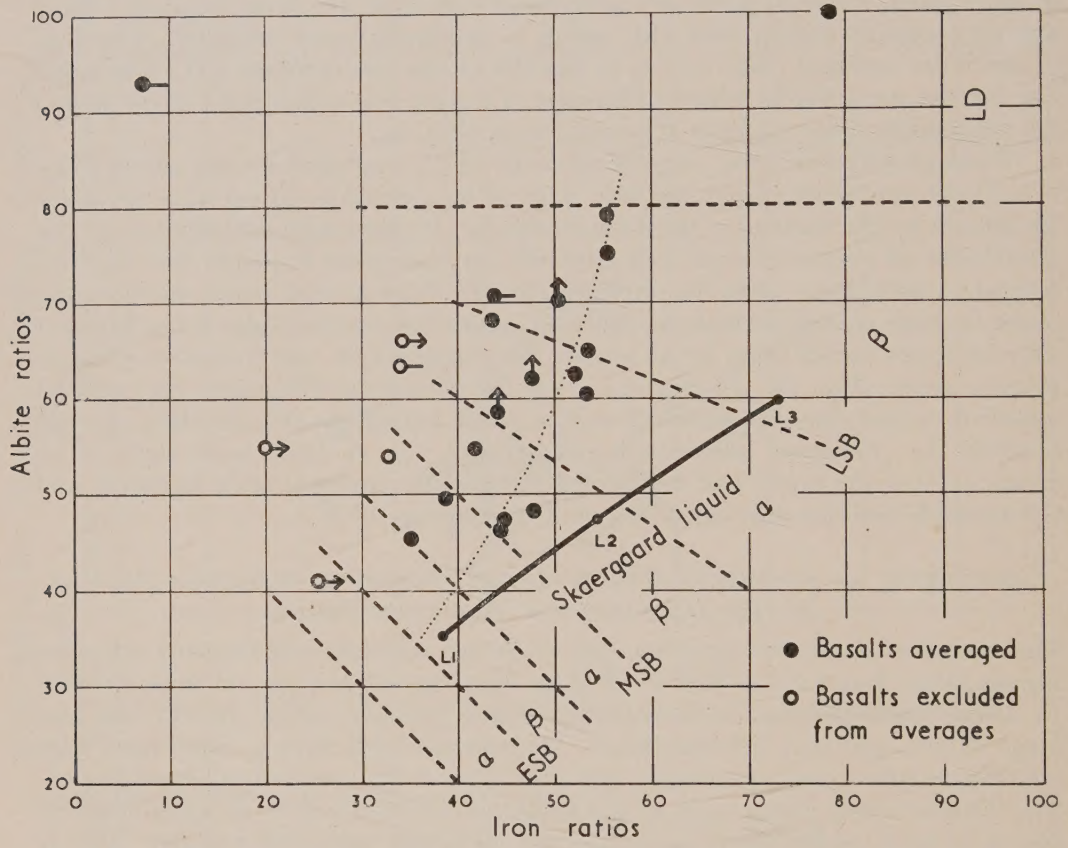


Fig. 3. Hawaiian Alkaline magma series divided into fractionation stages. Arrows or lines point to the probable position of the point if no phenocrystic accumulation or post-fractionation oxidation had occurred.

declining stage of volcanic activity. The characteristic lavas of these are more variable, consisting often of porphyritic basalts, and andesine and oligoclase basalts and trachyte, which are obvious later differentiates. Thus the field observers distinguish two stages in the development of the volcanoes, and these are correlated with characteristic lava types.

By means of differences in the pyroxenes of the Hawaiian basalts, and with the help of a plot of total alkalis against silica percentage, Tilley (1950) showed that there are two magma series in Hawaii, for which he uses the terms Tholeiitic and Alkaline (see below for discussion of this nomenclature); the former includes the primitive basalts of other Hawaiian investigators, and the latter

the declining-stage basalts. POWERS (1955) also divided the lavas into two major types, and then went further, breaking down the primitive lavas into various batches having special characteristics, particularly of silica and alkali content. Variation in the amount of olivine phenocrysts, believed to be due to sinking of olivine, causes a certain type of variation within each batch of basalts, but it is not such as to bridge over the differences between the various batches which POWERS establishes. He particularly defines batches of Mauna Loa and Kilauea primitive lavas, and distinguishes these from the declining-stage lava-types of Hualalai, Mauna Kea, and Kohala.

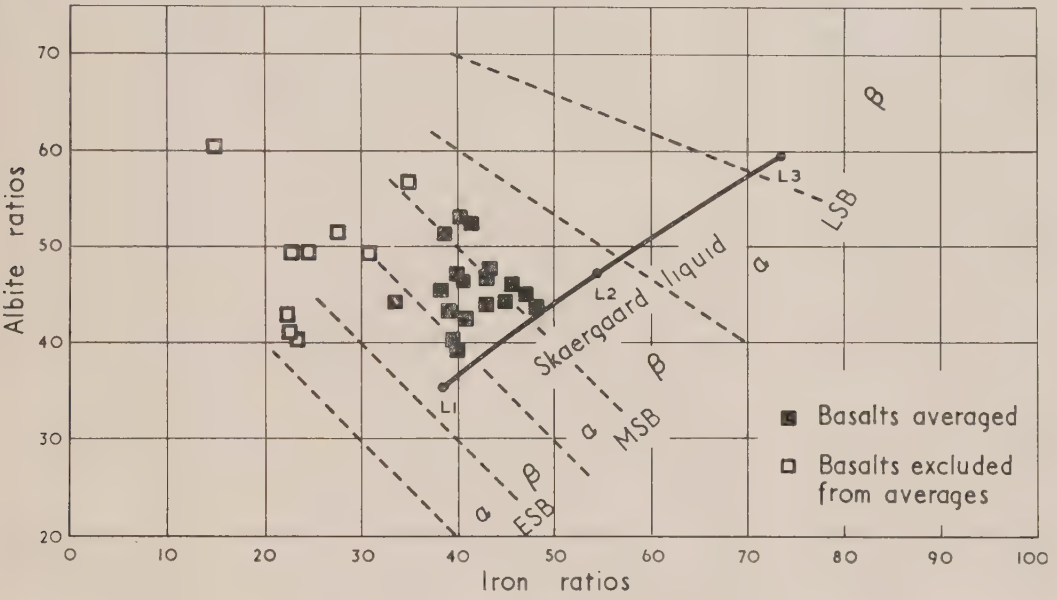


Fig. 4. Hawaiian Tholeiitic basalts (all good analyses of lavas from Kilauea and Mauna Loa given by MACDONALD) divided into fractionation stages.

The twofold division of the Hawaiian lavas into the Tholeiitic primitive basalts of Mauna Loa and Kilauea, and the Alkaline series—the so-called declining-phase basalts—seems well established and is accepted here. The two series are separately plotted in Figs. 3 and 4 to show to what extent they may be divided into differentiation stages. All satisfactory analyses of lavas from Hualalai, Mauna Kea, and Kohala are plotted in Fig. 3 except one (MACDONALD 1949a, p. 87. No. 9) which belongs to the Tholeiitic type. Fig. 4, showing the Hawaiian Tholeiitic basalts, includes all satisfactory analyses from Mauna Loa and Kilauea. From the descriptions it would appear that Tholeiitic basalts are also present on Kohala, although none have so far been analysed. Excluding the olivine-enriched picrite basalts, the Tholeiitic basalts are seen to be all at the early-stage β or middle-stage. Judged by chemical criteria, there is little crystal fractionation except that due to accumulation of early olivine to give the picrite basalts. There seems no reason why the Tholeiitic magma should not fractionate, given the appropriate conditions, but at Mauna Loa and Kilauea it has not done so to any extent. In contrast, the Hawaiian Alkaline series (Fig. 3) shows a succession

of stages from middle to late stage basalts and finally to late differentiates, which correspond to the differentiation trend from olivine basalt, through andesine and oligoclase basalts to trachytes, established by previous workers.

The average composition of the basalts of the two series at different stages of fractionation has been obtained by averaging the actual analyses of the basalts falling into the different stages, and near the general trend line (Table 1).

Table 1. *Averages at successive fractionation stages of Hawaiian basalts belonging to the Alkaline and Tholeiitic series*

Fractionation stage	*Early stage*	*Middle stage*				*Late stage*		*Late differentiates*
	β	*α*		*β*		*α*	*β*	*Trachyte*
Magma type	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Alk.*	*Alk.*
Numbers averaged	3	2	8	4	7	5	5	2
SiO_2	*50·8*	46·1	*51·2*	47·7	*50·9*	49·0	50·6	62·1
Al_2O_3	*13·1*	13·5	*13·0*	15·8	*12·8*	16·6	15·9	18·1
Fe_2O_3	*3·6*	3·4	*1·7*	3·7	*2·3*	3·0	3·9	3·0
FeO	*8·2*	9·3	*9·5*	8·7	*9·5*	8·4	7·7	1·4
MgO	*7·5*	8·7	*7·5*	5·9	*7·2*	4·8	3·9	0·4
CaO	*10·3*	10·0	*10·7*	11·0	*10·3*	8·1	7·4	0·9
Na_2O	*2·0*	2·4	*2·2*	2·9	*2·4*	4·1	4·8	7·6
K_2O	*0·4*	0·8	*0·4*	0·8	*0·5*	1·6	1·8	5·0
H_2O^+	*0·6*	1·3	*0·2*	0·4	*0·2*	0·6	0·4	0·6
H_2O^-	*0·4*	0·6	*0·1*	0·1	*0·1*	0·2	0·1	0·2
TiO_2	*3·0*	4·0	*3·1*	2·7	*3·2*	3·0	2·9	0·3
P_2O_5	*0·2*	0·4	*0·3*	0·4	*0·3*	0·9	0·7	0·2
MnO	*0·1*	0·1	*0·1*	0·1	*0·1*	0·2	0·1	0·2

Analyses of Tholeiitic basalts at the early-β and middle stages are fairly numerous, and the averages are no doubt reasonably satisfactory. Unfortunately, there are less of the Alkaline series analyses falling into the various fractionation stages, and in most cases the averages can only provide a rough indication of the composition of the successive fractionation stages.

The Tholeiitic basalts are all at, or near to the middle stage α and show little chemical variation. The Alkaline magma series begins in the middle stage, and in composition is seen to be significantly different from that of the Tholeiitic series at the corresponding stage; in particular, the Alkaline magma basalt is lower in SiO_2, slightly richer in Al_2O_3 and alkalis, and appreciably more oxidized. In the successive fractionation stages the silica percentage rises fairly regularly, and thus the variation diagram plotted against silica percentage as given by

Macdonald (1949a, p. 83) for Mauna Kea is essentially the same as the variation shown by the successive fractionation stages. The general trend of the plotted points on the albite and iron ratio diagram (Fig. 3) is somewhat different from that of the Skaergaard magma, being steeper; this may partly correspond to the more oxidized state of the Hawaiian basalts compared with the Skaergaard magma.

Composition at Successive Fractionation Stages of Hebridean Basalts of the Alkaline and Tholeiitic Series

The authors of the Mull Memoir (Bailey, Clough, Richey, Thomas, *et al.*), were the first to use the terms magma type and magma series in a precise way (1924, p. 13). They reached the conception of a unified type partly from geological field evidence such as the manner of occurrence in place and time, and partly from certain mineralogical and textural characters determined in the laboratory. Having reached the conception of a magma type, they made an estimate based on analyses of carefully selected rocks of the average composition of the magma type, and such averages have been important standards of comparison ever since. The authors of the Mull Memoir then took the further step of grouping the magma types into series to show their presumed genetic relationships, the variation in composition of the magma series being expressed in variation diagrams against SiO_2 percentage.

The two most important basalt magma types defined in Mull were the Plateau magma and the Non-porphyritic Central magma types. In one form or another these have dominated ideas of petrogenesis for nearly three decades, not a little of the reason for this being Kennedy's further discussion of the magma types and their trends of differentiation. Kennedy (1931, 1933) accepted the concept of two main basalt magmas, the Plateau magma and the Non-porphyritic Central magma types, as valid for the Hebridean province, and attempted, with the help of other analyses, especially Washington's, to decide how far the composition of basalts of other regions fitted into these types. He considered that the Non-porphyritic type, which he renamed Tholeiitic, was the fundamental world type (1931, p. 67), and that it was probably the parent magma of the Hebridean province. In his later paper, however, he considered that for practical purposes the Plateau magma type, renamed the olivine basalt magma type, was to be regarded also as a world type of the same status, and independent of the Tholeiitic magma type (1933, p. 242).

The magma types of Mull were arranged by the authors of the Memoir in magma series on the basis of all available lines of evidence, including particularly the field relations. It was considered that from the Plateau magma could be developed mugearites and trachytes, and this series, named the Alkaline magma series, was believed to result from crystal fractionation. Another series, the Normal Mull magma series, began with the Plateau magma type, passed through the Non-porphyritic Central magma type, and then through certain intermediate rocks to granite. The authors left open the question of the mechanism of formation of this series; on the whole, they thought of it as the result of crystal fractionation, but they did not exclude contamination and remelting as possible factors (1924, pp. 31, 32, 33). Kennedy accepted the Alkaline magma series as originating by

fractionation from the Plateau magma basalts (his olivine basalt), and gave additional petrological evidence for this; he also thought that the series might be extended to the phonolites. From the Non-porhyritic Central magma type (his Tholeiite), he thought, like the authors of the Mull Memoir, that intermediate and acid rocks might be developed, but he believed the process to be definitely one of crystal fractionation from the more silica-rich Tholeiitic magma. Later, Kennedy and Anderson (1938) returned to a consideration of the relationship of the two main basalt magma types, and postulated that the Plateau and Tholeiitic magmas are essentially independent, being derived from two distinct earth shells. Although Kennedy based a system of petrogenesis on the two basalt types first defined in Mull, yet the compositions of the parent magmas have never been very satisfactorily defined: indeed, the average compositions given originally by the authors of the Mull Memoir were accepted by Kennedy and others as adequate, or at any rate as the best obtainable.

When an attempt is made to extend the Mull basalt types into world types, the definition and nomenclature become confused—which is not unexpected, since there is no clarity about the nature of the things which are being named. The original name Plateau magma basalt was used in a fairly precise way by the authors of the Mull Memoir, who gave its mineralogical and chemical characteristics. Kennedy (1931, 1933) attempted to show that a magma type generally, like the Plateau magma of Mull, was widespread throughout the world, but he also showed at the same time that many of the extensive basalt plateau areas of the earth were composed of basalts having affinities with the Non-porphyritic Central type of Mull. He therefore felt that the term Plateau magma was unsatisfactory, and introduced the descriptive name olivine basalt magma. This has proved even less satisfactory, and Tilley in his recent presidential address to the Geological Society of London (1950) avoided the use of this term on the grounds that it is too wide an appellation. Tilley has used instead the term alkali basalt for what is the old Plateau magma type of Mull, and this term, or the original term, Plateau magma basalt, is used in this paper.

The other important basalt type defined in Mull was given the rather unwieldy name of Non-porphyritic Central type. This was changed by Kennedy without modifying its meaning to Tholeiitic magma type. There are objections to this name, as Wells and Wells have pointed out (1948, p. 353–4). It has, however, been widely accepted (compare Tilley, 1950, p. 41, and Holmes, 1949; and textbooks such as Turner and Verhoogen, 1951), and it has the convenience of greater brevity than the original name proposed for the Mull examples. In this paper, the terms Tholeiitic basalt and Tholeiitic magma series are used, although they are not ideal. The extent to which basalts from other parts of the world can usefully be classified as of Tholeiitic or Plateau magma type is considered in a later section.

By arranging the Hebridean analyses into fractionation stages, and then averaging, it is believed that a better conception of the composition of the Plateau and Tholeiitic magma types can be obtained, and, at the same time, of the variation in composition of the differentiation series to which they give rise. An albite and iron ratio plot (Fig. 5) has been prepared of all satisfactory analyses of the lavas

of the Hebridean province, including Northern Ireland (for which there are several new analyses by TOMKEIEFF and PATTERSON). The analyses are listed in Appendix 2, and the co-ordinates there given for each will allow any particular point to be identified. The lavas are classified by symbols into Plateau magma basalts, mugearites and trachytes forming the Alkaline magma series. Tholeiitic basalts

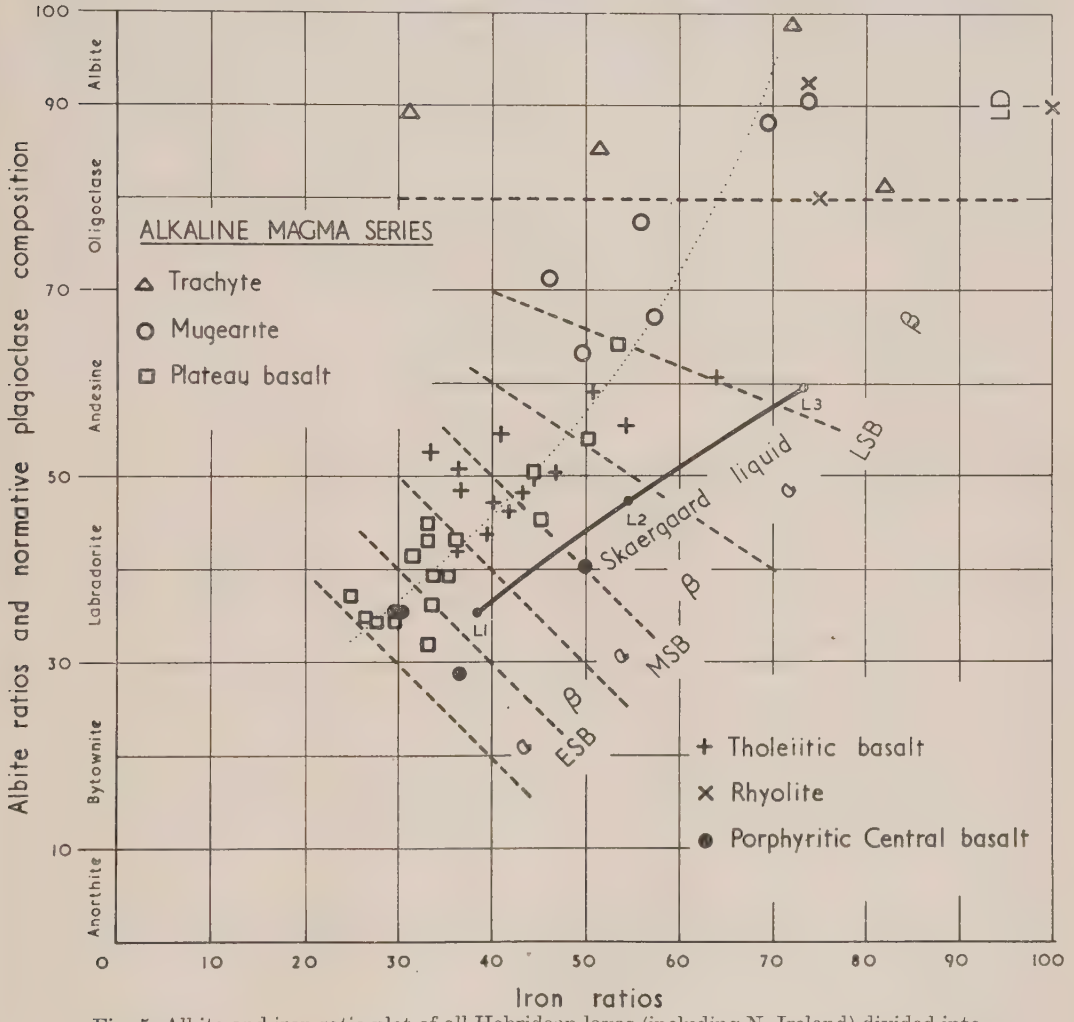


Fig. 5. Albite and iron ratio plot of all Hebridean lavas (including N. Ireland) divided into fractionation stages.

and rhyolites, and finally, Porphyritic Central type basalts, which, however, are not considered in any detail, as there are so few analyses available. The spread of points is divided into the same fractionation stages as the Hawaiian, and average compositions of the lavas of the various types at the successive stages have been calculated (Table 2).

The classification of the Hebridean basalts into Plateau and Tholeiitic magma types used for the albite and iron ratio plot (Fig. 5) is the one given by the various

investigators concerned, and it is therefore based partly on the petrological and mineralogical characteristics and partly on the chemical composition. The original authors classification has also been used in calculating the averages (Table 2). Comparison of the averages for the Alkaline and Tholeiitic basalts at the different stages gives the chemical differences, accepting the original classification, which exist between the two series. Tilley (1950, p. 42) in discussing Hawaiian lavas, showed that a plot of alkalis against silica provides a graphical method of dividing basalt analyses into those belonging to the Alkaline and the

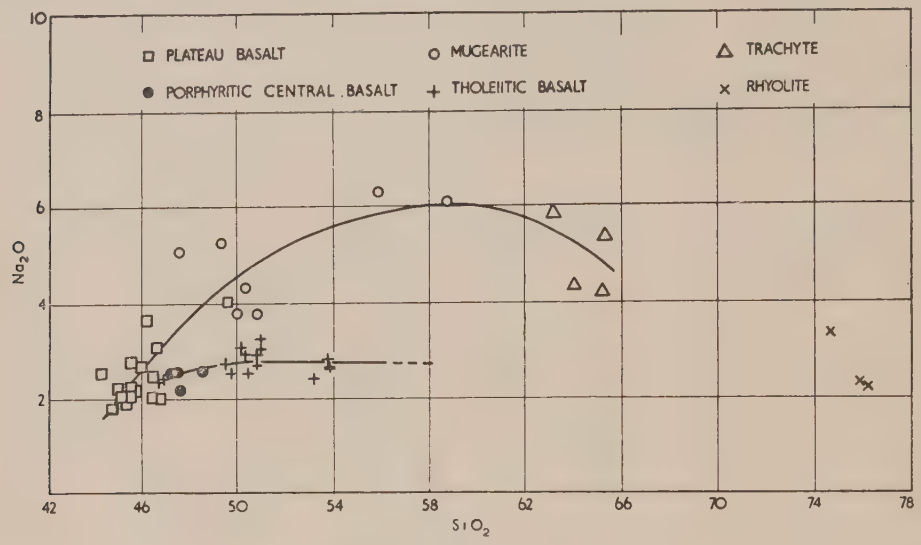


Fig. 6. Silica-soda plot for Hebridean basalts showing the distinction into Alkaline and Tholeiitic types.

Tholeiitic series. For the Hebridean area a similar plot of soda (not total alkalis) against silica gives again satisfactory division into the two series (Fig. 6). Thus chemical criteria could be used for dividing basalts roughly into the Alkaline and Tholeiitic series, but in the present paper the division as given by original authors has been used.

The Alkaline magma series shows the same general trend on the plot (cf. Figs. 3 and 5) and in the composition of the rocks at the various stages, as that series in Hawaii (cf. Tables 1, 2, and 4). For the Hebrides, however, there are several analyses representing earlier stages than are so far known from Hawaii. Throughout the early, middle, and late stages of the Hebridean Alkaline magma series the silica percentage remains low. Comparison with the fractionation of the Skaergaard magma would suggest that during the early and middle stages 80 or 90 per cent of the original magma must have crystallized. Over this extensive crystallization period the amount of SiO_2 has only changed from 45 to 50 per cent, while Na_2O has changed from 2 to 5 per cent and K_2O from 0·3 to 1·5 per cent.

Trace-element analyses of the Northern Ireland Plateau magma basalts have been made by Patterson (1951, p. 290) and similar data on the middle- and late-stage basalts and late differentiates for the Alkaline series in Scotland have been

Table 2. Averages at successive fractionation stages of the Hebridean basalts belonging to the Alkaline and Tholeiitic series

Fractionation stage	*Early stage*			*Middle stage*				*Late stage*				*Late differentiates*		
	α	β		α		β		α		β		*Mugearite*	*Trachyte*	*Rhyolite*
Magma type	*Alk.*	*Alk.*	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Thol.*	*Alk.*	*Alk.*	*Thol.*
Numbers averaged	6	6	1	—	6	2	4	3	2	3	1	2	4	3
SiO_2	45·6	45·5	*46·7*		*50·0*	46·0	*51·3*	48·8	*50·7*	48·9	*53·8*	57·2	64·4	*75·5*
Al_2O_3	15·1	15·0	*14·5*		*14·3*	15·6	*14·2*	15·6	*13·8*	15·2	*12·8*	16·5	15·0	*12·3*
Fe_2O_3	3·3	3·1	*3·3*		*3·0*	3·6	*3·1*	5·4	*3·2*	5·5	*3·4*	3·1	3·5	*0·8*
FeO	7·8	9·3	*8·7*		*7·3*	10·4	*7·9*	8·3	*8·8*	8·0	*8·9*	5·5	2·5	*0·4*
MgO	10·6	10·0	*8·4*		*6·6*	6·9	*5·6*	4·3	*4·4*	3·7	*2·6*	1·1	0·8	*0·1*
CaO	10·3	9·3	*11·9*		*10·9*	8·7	*9·9*	7·5	*8·9*	6·3	*6·6*	3·1	1·7	*0·8*
Na_2O	1·9	2·4	*2·4*		*2·6*	2·9	*2·7*	3·7	*3·0*	4·7	*2·7*	6·2	4·9	*2·7*
K_2O	0·3	0·3	*0·1*		*0·8*	0·6	*1·2*	1·3	*1·2*	1·5	*2·3*	3·7	4·6	*4·6*
H_2O^+	2·3	2·3	*0·2*		*0·9*	1·5	*1·0*	1·3	*2·6*	1·3	*2·2*	0·8	0·8	*1·7*
H_2O^-	1·3	0·8	*0·4*		*1·8*	0·9	*1·6*	1·4	*0·7*	1·7	*1·2*	0·9	0·4	*1·0*
TiO_2	1·2	1·9	*0·6*		*1·1*	2·8	*1·1*	2·4	*2·0*	2·2	*2·4*	1·3	0·6	*0·1*
P_2O_5	0·2	0·2	*0·1*		*0·4*	0·3	*0·4*	0·3	*0·5*	0·8	*0·6*	0·5	0·2	—
MnO	0·2	0·2	*0·2*		*0·2*	0·3	*0·2*	0·3	*0·2*	0·3	*0·5*	0·2	0·2	—

provided by Nockolds and Allen (1954, p. 254). From these data, average compositions have been obtained for the various fractionation stages (Table 3). The changes in the trace elements show the same pattern as the Skaergaard Intrusion (Wager and Mitchell, 1951), which is accepted as certainly the result

Table 3. Trace elements in Hebridean basalts and differentiates arranged in fractionation stages

	Alkaline magma series					*Tholeiitic magma series*		
	Ireland		*Scotland*			*Ireland*		
Fractionation stage	*E.S.α*	*E.S.β*	*M.S.β*	*L.S.*	*L.D.*	*E.S.β.*	*M.S.α.*	*M.S.β.*
No. of rocks analysed	4	2	2	4	4	1	5	2
P	900	1100	1200	3300	2000	1400	2000	2800
Ga	30	40	20	25	20	20	25	25
Cr	2000	900	100	*	*	500	130	40
V	700	550	200	90	*	400	500	400
Li	9	6	20	90	40	3	10	7
Ni	950	850	80	*	*	100	50	30
Co	140	150	30	20	*	50	40	40
Cu	500	250	—	—	—	200	150	70
Sc	20	18	20	*	*	20	25	30
Zr	200	170	100	290	540	60	250	120
Mn	1300	1400	2300	2700	1550	1700	1400	1700
Y	50	50	30	35	45	30	50	40
La	*	*	*	*	90	*	*	*
Sr	450	650	450	800	650	300	500	500
Ba	300	300	200	950	2250	20	400	400
Rb	5	*	10	50	130	1	15	10

Data for Ireland from Patterson and Swaine. Data for Scotland from Nockolds and Allen.
* Indicates less than the sensitivities which are approximately: Cr, 1; V, 5; Ni, 2; Co, 2; Cu, 1; Sc, 10; La, 30; Rb, 3.

of crystal fractionation. The trace-element compositions at the primary and early stages found for the Irish part of the Hebridean province fit on to the later sequence of changes shown by the Scottish data, although detailed comparison should not be made, as the data from the two areas were obtained by different investigators using somewhat different methods. Regularities in the variation in the trace constituents are most marked where fractionation is having a strong effect on the amount of the particular element; for example, chromium and nickel in the early stages; vanadium, cobalt, and strontium in the middle stages; barium and rubidium, and to some extent lithium, zirconium, and lanthanum, in the later stages. Using these elements as appropriate, an assessment could be made of the stage of fractionation.

The Hebridean Tholeiitic series so far identified begins, as in Hawaii, in the early-stage β, but lavas ascribed to it extend to the late-stage, a wider range than in Hawaii. Thus there is apparently more fractionation of the Tholeiitic magma in the Hebrides. Two analyses of different parts of flow 2 at the Giant's Causeway, Northern Ireland (Tomkeieff, 1940), show a range from middle-stage β to late-stage α. It is surprising that so considerable a range is shown by a single flow; the earlier-stage rock is, however, from the colonnade, while the later is from the entablature; if differentiation had occurred at all it would be expected that the upper rock would be the later fraction (Tomkeieff, 1940, p. 111–2).

There are also trace-element data for the Northern Ireland Tholeiitic magma series by Patterson and Swaine (1955) who provide data for nine basalts, five of which fall into the middle-stage α. Some degree of crystal fractionation is indicated, particularly by chromium, nickel, zirconium, and barium. Comparison between the trace-element composition of the Alkaline and Tholeiitic series shows that there is little difference at the middle stage α, the only stage when satisfactory comparisons can be made. The average trace-element composition given for Hawaiian basalt (Wager and Mitchell, 1953, Table 2) represents values for basalts of the Tholeiitic series, and is close to the composition of middle-stage Tholeiitic magma from Northern Ireland (Table 3).

In both the Alkaline and Tholeiitic series the variation in the amounts of the various oxides at successive stages is smooth. Although the trend in the figures for FeO, MgO, Na_2O and to some extent, CaO are directly the result of the method of selection, the trend in the amounts of other oxides, SiO_2, K_2O, TiO_2, P_2O_5, are not, and their variation, especially in the Alkaline series, is such as would be expected to result from crystal fractionation. For the Alkaline series, as in the Skaergaard example of fractional crystallization, SiO_2 and K_2O increase throughout, while FeO, TiO_2 and P_2O_5 reach maxima.

If the validity of the original investigators' division of the Hebridean basalts into Plateau and Tholeiitic types is accepted then the results here given (Table 2 and Fig. 7) show the chemical differences at successive fractionation stages. The most important chemical distinction between the series is the higher SiO_2 percentage in the Tholeiitic series which is the usually accepted distinction but it becomes more certain when compositions at similar fractionation stages are compared. There are other chemical differences which hold good for the particular area but may not be generally true; thus at corresponding stages the Tholeiitic series (cf. Fig. 7) is poorer in alumina, richer in lime, and poorer in TiO_2. These distinctions are valid for the Hebridean Alkaline and Tholeiitic basalts but it may fairly be asked whether they are equally significant for other areas. In an attempt to answer this a preliminary estimation of the composition at successive fraction stages of basalts from other areas is given in the following section.

Comparison at Similar Fractionation Stages of Basalts from Various Localities

The existence of a layer of basaltic rocks within the earth is generally accepted, and one of the interesting and fundamental problems of geology is the question

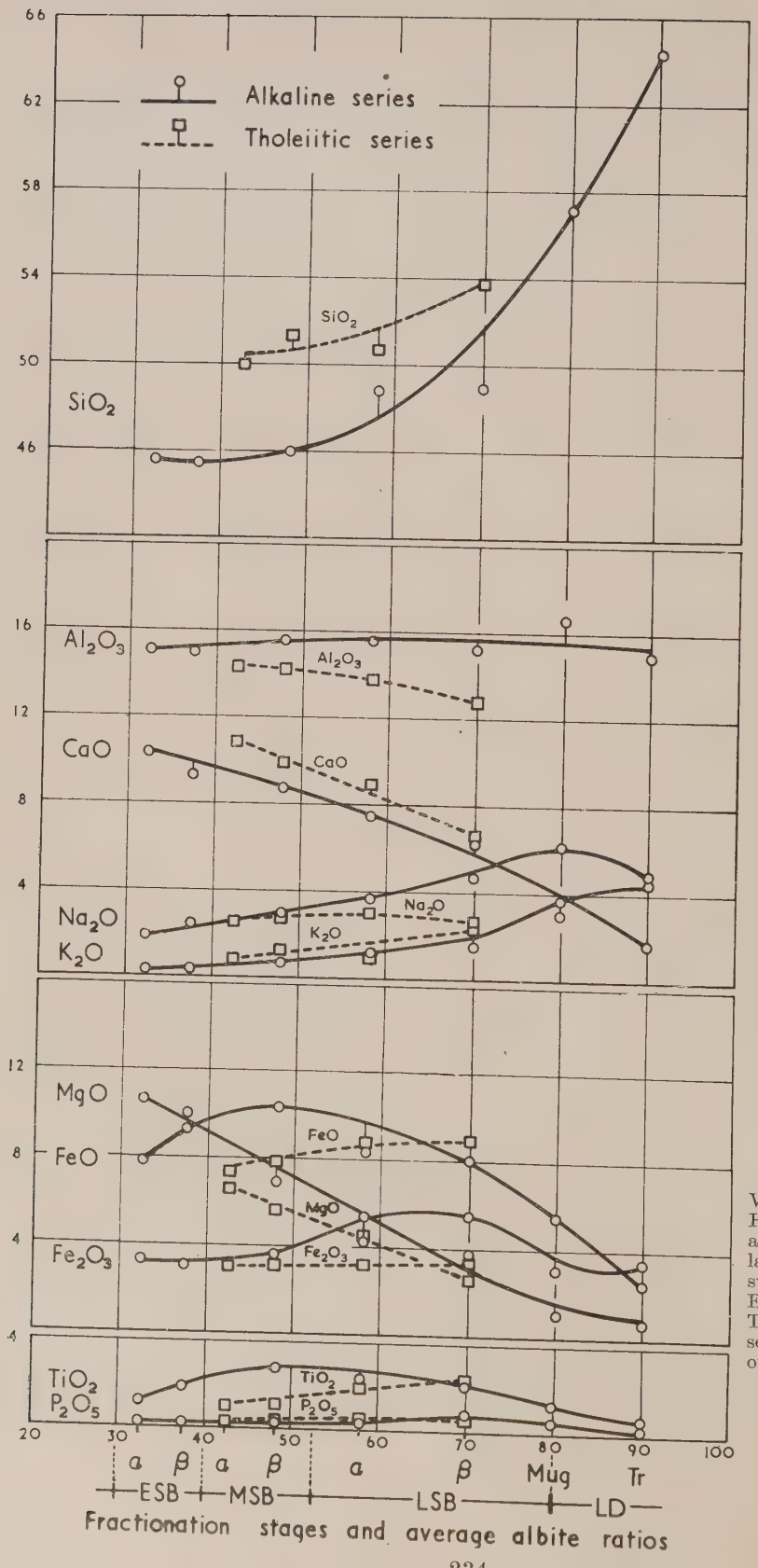


Fig. 7.
Variation diagram for Hebridean Alkaline and Tholeiitic series lavas, plotted against stage of fractionation. Early stage β of the Tholeiitic series, represented by one analysis only is not plotted.

whether there are any overall chemical differences in the composition of the basalt layers in different parts of the earth. In the basalts and plutonic equivalents which the geologist examines there is so much chemical variation due to fractionation and other causes, that straight averages of the analysed basalts and related rocks of any region such as recently provided by GREEN and POLDERVAART (1955) do not give any great confidence for the belief in a fundamental heterogeneity of the basalt layer of the earth. Using the breakdown into fractionation stages, however, there is a better indication of certain chemical differences which are believed to be of significance.

Comparison of the Hawaiian and Hebridean Alkaline basalts can conveniently be made with the help of Table 4. There is an overall similarity justifying grouping them both together as belonging to the Alkaline series, but in the Hawaiian basalts, CaO and TiO_2 at corresponding stages are higher than in the Hebridean series, and other slighter differences are suggested by the averages. It seems probable that the slight differences in the early stages are responsible for some of the more obvious differences in the trachytic end-products. By graphing the composition of various Alkaline series of basalts on the magnesium, iron, and alkali triangular diagram, NOCKOLDS and ALLEN (1955) obtain slightly different trends suggesting significant differences. It seems possible that other characteristic chemical differences will appear when the average amounts of certain trace elements at the various stages are better known.

Considering the Tholeiitic series of Hawaii and the Hebrides (Table 4), the high SiO_2 of both series, justifying grouping them as of Tholeiitic type, may first be noted. Further comparison of the averages shows that there are minor differences, for example the Hebridean rocks in the middle stages are richer in Al_2O_3, Na_2O and K_2O and poorer in TiO_2 than the Hawaiian and these differences are probably significant. Lower TiO_2 is a feature of both the Tholeiitic and Alkaline Hebridean basalts and is apparently characteristic of the province. The available evidence on the trace elements for the tholeiitic series is even slighter than for the Alkaline; PATTERSON'S figures for the trace elements in the Tholeiitic series of Northern Ireland, however, are so different from those for the few Hawaiian Tholeiitic rocks analysed (WAGER and MITCHELL, 1953, Table 2, column 2) that perhaps real differences exist.

How closely do basalts from other regions fall fairly into the Alkaline and Tholeiitic magma series, and at the same time how certainly do minor chemical differences within each series characterize particular areas or petrographic provinces? POWERS (1955) shows that even in Hawaii it is profitable to regard the contemporaneous Tholeiitic magma of Kilauea as belonging to a significantly different batch from that of Mauna Loa. As satisfactory analyses increase, we shall no doubt find it valuable to pick out such detailed consanguineous groups and then classify them into the broader grouping of the Tholeiitic or Alkaline magma series on the basis of silica percentage without however anticipating exact similarity with this series in the Hebridean type area.

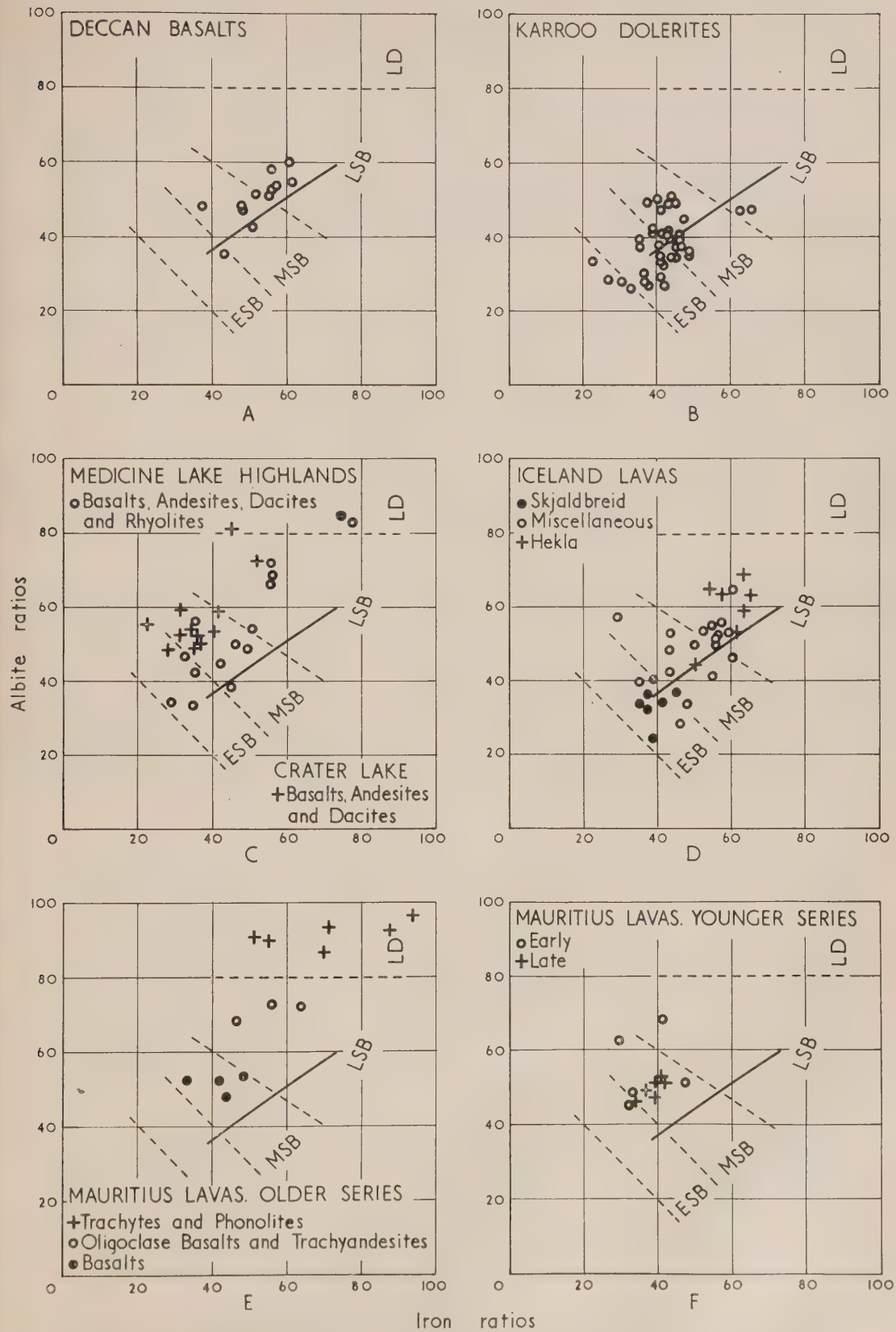
The Deccan lavas are represented by twelve good analyses (WASHINGTON, 1922; FERMOR, 1934) and of these, five fall into the middle stage and six into the late stage (Fig. 8a). Averages for these two main stages are given in Table 5.

Table 4. Hebridean and Hawaiian Alkaline and Tholeiitic series compared

		Alkaline Series							*Tholeiitic Series*					
	Fractionation stage	*Early stage*		*Middle stage*		*Late stage*		*Late differentiates*		*Early stage*	*Middle stage*		*Late stage*		*Late differentiates*
		α	β	α	β	α	β	*Mugearite*	*Trachyte*	β	α	β	α	β	*Rhyolite*
	Fe Ratio	32½	37½	42½	48	55	62			37½	42½	48	55	62	
	Ab Ratio	32½	37½	42½	48	57	70			37½	42½	48	57	70	
	Numbers averaged	6	6	—	2	3	3	2	4	1	6	4	2	1	3
HEBRIDEAN	SiO_2	45½	45½		46	49	49	57	64	46½	50	51½	50½	54	75½
	Al_2O_3	15	15		15½	15½	15	16½	15	14½	14½	14	14	13	12½
	Fe_2O_3	3½	3		3½	5½	5½	3	3½	3½	3	3	3	3½	1
	FeO	8	9½		10½	8½	8	5½	2½	8½	7½	8	9	10	½
	MgO	10½	10		7	4½	3½	1	0·8	8½	6½	5½	4½	2½	0·1
	CaO	10½	9½		8½	7½	6½	3	1·8	12	11	10	10	6½	0·8
	Na_2O	1·9	2·4		2·9	3·7	4·7	6·2	4·9	2·4	2·6	2·7	3·0	2·7	2·7
	K_2O	0·3	0·3		0·6	1·3	1·5	3·7	4·6	0·1	0·8	1·2	1·2	2·3	4·6
	TiO_2	1·2	1·9		2·8	2·4	2·2	1·3	0·6	0·6	1·1	1·1	2·0	2·4	0·1
	P_2O_5	0·2	0·2		0·3	0·3	0·8	0·5	0·2	0·1	0·4	0·4	0·5	0·6	0·01
	Numbers averaged			2	4	5	5		2	3	8	7			
HAWAIIAN	SiO_2			46	47½	49	50½		62	51	51	51			
	Al_2O_3			13½	16	16½	16		18	13	13	13			
	Fe_2O_3			3½	3½	3	4		3	3½	1½	2½			
	FeO			9½	8½	8½	7½		1	8	9½	9½			
	MgO			8½	6	4½	4		½	7½	7½	7			
	CaO			10	11	8	7½		1	10	10½	10½			
	Na_2O			2·4	2·9	4·1	4·8		7·6	2·0	2·2	2·4			
	K_2O			0·8	0·8	1·6	1·8		5·0	0·4	0·4	0·5			
	TiO_2			4·0	2·7	3·0	2·9		0·3	3·0	3·1	3·2			
	P_2O_5			0·4	0·4	0·9	0·7		0·2	0·2	0·3	0·3			

Mull averages (1924)

	Plateau basalt	*N.P.C basalt*
SiO_2	45	50
Al_2O_3	15	13
FeO, Fe_2O_3	13	13
MgO	8	5
CaO	9	10
Na_2O	2·5	2·8
K_2O	0·5	1·2



Figs. 8A, B, C, D, E, and F. Albite and iron ratio plots of basic rocks from the Deccan, Karroo, Medicine Lake Highland, Crater Lake, Iceland, and Mauritius. The continuous line in all the graphs is the Skaergaard Intrusion trend for the early and middle stages

Table 5. Comparisons at various fractionation stages of averag

	Hebridean Tholeiitic Series		*Deccan Basalts*		*Karroo Dolerites*			*Mull Basalts P.C. type*	*Skaergaard*	
									Original magma	*2nd liquid*
Fractionation stage	*M.S.*	*L.S.*	*M.S.*	*L.S.*	*P.S.*	*E.S.*	*M.S.*	*E.S.*	*E.S.*	*M.S.*
Numbers averaged			5	6	4	13	19	3		
SiO_2	50½	53	50	50½	49½	52	52	48	48	47
Al_2O_3	14½	13½	13	13	15	15½	15	20	19	15
Fe_2O_3	3	3	4	3	1	1	1	4½	1	3
FeO	8	9	9½	11	8½	9	9½	4	9	13
MgO	6	3½	6	4½	12½	7½	6½	5	8	6
CaO	10½	7½	10	9½	10	10½	10	12½	10½	10
Na_2O	2·6	2·8	2·3	2·9	1·7	1·8	2·4	2·4	2·4	2·8
K_2O	1·0	2·0	0·6	0·8	0·5	0·6	0·9	0·3	0·2	0·3
TiO_2	1·2	2·2	2·8	1·9	0·6	0·9	1·2	1·3	1·3	2·2
P_2O_5	0·4	0·6	0·3	0·4	0·08	0·12	0·15	0·3	0·1	0·4

Notes: The figures for Hebridean Tholeiitic series at the middle stage are smoothed averages from graph, Fig. Deccan: Washington (1922) Fermor (1934). Karroo: Walker and Poldervaart (1949). Mull: The averag given is for three Porphyritic Central basalts, Bailey *et al.* (1924, p. 24). Skaergaard: Wager and Deer (193 Table XXXVI). Medicine Lake Highland, Calif.: Average of three sub-ophitic basalts, Anderson (1941, p. 88 Nos. 1, 2 and 3). Iceland: Skjaldbreid basalts, Tryggvason (1943, p. 313, No. 1). Hekla: Average of two basalt

They show considerable similarity with the differentiated Hebridean Tholeiitic series.

Some of the fine chemical data now available for the Karroo dolerites (Walker and Poldervaart, 1949) have also been examined, although these rocks are intrusive sills and most of this paper is concerned with the lavas. The justification for their consideration in the present paper is the great similarity between the few Stormberg lavas that have been analysed and the more abundant data for the Karroo dolerite sills. The albite and iron ratio plot for all except the extreme types of Karroo dolerites (Fig. 8b) shows a contrast with the Deccan lavas, there being many more examples of earlier stage basalts in the Karroo. Apparently also the amount of fractionation of the Karroo magma which has occurred is limited, as with the Tholeiitic series in Hawaii. The several types defined by Walker and Poldervaart were grouped into three for the purposes of the original plot, and it was seen that the Kokstad type was on the whole the earlier: but for the purpose of defining the composition at various fractionation stages

compositions of basalts and related rocks from various provinces

Medicine Lake Highland Basalts		*Iceland Basalts*		*Mauritius*				*Hebridean Alkaline Series*		
				Older Series			*Late Younger Series Basalt*			
		Skjaldbreid	*Hekla*	*Basalt*	*Olig basalt Trachyandesite*	*Trachyte*				
*E.S.**	*M.S.*	*E.S.*	*L.S.*	*M.S.*	*L.S.*	*L.D.*	*M.S.*	*E.S.*	*M.S.*	*Fractionation stage*
3	5	6	2	4	3	6	6			*Numbers averaged*
48	53	47½	55	46	52	63	46	45½	46	SiO_2
19	19	14	16	14½	16½	19	15	15	15½	Al_2O_3
1	2	2½	2½	4	4½	2½	3	3	3½	Fe_2O_3
8	6½	10	9½	8½	6	2	10	8½	10½	FeO
9	4½	9	3	7	2½	0·4	9	10	8	MgO
11	9	12½	7	10	6	1·5	11	10	9	CaO
2·5	3·2	1·7	3·6	2·8	4·7	6·9	2·9	2·0	2·5	Na_2O
0·2	1·1	0·3	0·9	1·1	2·6	4·9	0·6	0·3	0·6	K_2O
0·9	1·0	2·0	1·6	3·3	2·1	0·2	2·5	1·6	2·7	TiO_2
0·1	0·1	0·2	0·4	0·4	0·6	0·1	0·3	0·2	0·3	P_2O_5

Einarsson (1950, p. 34, Nos. 5 and 6). Mauritius: Walker and Nicolaysen (1954). Older Series Basalts, p. 41, Nos. 323, 350 ,and 275. Oligoclase basalt, p. 41, No. 56, Trachyandesites, p. 24, column 13, Trachytes, p. 24, column 15. Late Younger Series, Average basalt, p. 24, column 21. The figures for Hebridean Alkaline series at early and middle stages are smoothed averages from graph, Fig. 7.

* One analysis falls just within primary stage.

the distinction into the three petrographic types has been ignored (Table 5). As Walker and Poldervaart show, the average Karroo magma belongs to the Tholeiitic magma series as defined in Mull, having SiO_2 percentages of 49 to 52 even in the primary and early fractionation stages. Plotting also indicates that half of the analyses fall into earlier differentiation stages than are represented in the Hebridean province. Where comparison is possible, as in the middle stage, it is clear that the Karroo magma differs little from the Hebridean. Comparing the Hebridean, Hawaiian, Deccan, and Karroo Tholeiitic basalts, the most significant difference is that the Karroo exhibits much more abundant examples of the earlier fractionation stages than either of the other three. The Karroo magma is also markedly more reduced, but this is not regarded as the cause of the fractionation stage differences. It is of interest that the Karroo rocks (Fig. 8b) group themselves fairly symmetrically around the point for the original Skaergaard magma, which is also a strongly reduced type, as also are the early basalts of the Medicine Lake Highland (Table 5). The Karroo magma belongs to an earlier

fractionation stage, and therefore should be a higher temperature type of basalt than the Tholeiitic basalts so far identified in the Hebrides, Hawaii, or the Deccan. The characteristics of the Karroo magma are essentially those due to its early stage and high temperature, and these characteristics appear in the overall average of Karoo dolerites (Walker and Poldervaart, 1949, Table 17). The early, high-temperature characteristics of the rocks is also suggested by the triangular plot given by Walker and Poldervaart (1949, Fig. 27).

Because the course of differentiation for the Skaergaard magma is well established as the result of fractional crystallization, it is worth consideration here, although evidence for the composition of successive residual magmas is only indirect. As already mentioned (page 220), the second liquid composition, after 60 per cent of the original magma had crystallized, is probably a reliable estimate, while the composition of later liquids is of less value. The Skaergaard magma has high alumina reflected by richness in plagioclase. Lime, however, is not particularly high, because much of the ferromagnesian material is either olivine or inverted pigeonite, and not augite. The rocks do not fall into the Alkaline magma series, and fractionation does not produce trachytic late differentiates. On the other hand, they are not typically Tholeiitic, the results of fractionation leading to very high iron concentrations, which is not typical of the Tholeiitic series. Many basalts have a certain similarity with the original Skaergaard magma, as for example the Medicine Lake Highland basalts and the Mull Porphyritic Central basalts (Table 5). There is also some degree of similarity with the early basalts of the Hakone volcano described by Kuno (1950). As Tilley has argued (1950, p. 56), this type of magma is perhaps justifiably to be regarded as distinct from both the Alkaline and Tholeiitic magma types.

For Icelandic lavas there are now many satisfactory analyses which are plotted in Fig. 8d. It is clear that, in this extensive volcanic region, the rocks of which vary in age from early Tertiary to the present-day, there is a good deal of fundamental variation in the composition of the basalts and their differentiation products. Two examples will be considered; the Skjaldbreid volcano is built up of a rather constant type of lava, and of the seven analyses available (Tryggvason, 1943, p. 313) six fall into the early-stage. The average is given in Table 5, and is seen to be fairly close to the Hebridean early-stage Alkaline magma, but is higher in SiO_2 and CaO and lower in Al_2O_3, thus showing some affinity with the Tholeiitic magma type. The recent Hekla lava (Einarsson, 1950, p. 34) is an example of a basalt belonging to the late stage (Fig. 8c). In composition (Table 5) it resembles up to a point the late-stage Alkaline magma from the Hebrides, but is also is richer in SiO_2 and poorer in the alkalis, and so like the Skjaldbreid lavas has some Tholeiitic features. Thus some of the Icelandic lavas show features rather intermediate in character between the Hebridean Alkaline and Tholeiitic magma series.

In Mauritius, as shown by the data recently provided by Walker and Nicolaysen (1955), there is a region of basalts belonging to the Alkaline magma series. This is indicated by the relatively low SiO_2 and the nature of the products of fractionation, which include oligoclase basalts and trachytes. For the Mauritian Older Series (Fig. 8e and Table 5) the middle-stage basalts are slightly poorer

in Al_2O_3 and richer in CaO and alkalis than the middle stage Hebridean Alkaline basalts and similar features are shown by the Mauritian Late Younger series. The latter is essentially undifferentiated (Fig. 8f), all analysed examples falling within the middle fractionation stage. In Hawaii the Tholeiitic magma is found undifferentiated, while in Mauritius, during the whole volcanic episode to the Late Younger series, the Plateau magma remained undifferentiated.

Other oceanic islands such as Samoa and Jan Mayen show potash-rich basalt types, while yet others are characterized by high potash and soda together and develop strongly undersaturated lavas in the late stages of fractionation. These, together with the basalt-andesite-rhyolite series of orogenic regions, are some way removed from the Alkaline and Tholeiitic magma series and will not be considered here.

From these preliminary comparisons it seems that other basalts show an approach to the Hebridean Alkaline and Tholeiitic magma series, but that there are differences which become apparent when the rocks at comparable fractionation stages are considered. The Alkaline basalts are characterised chemically by having lower silica than the Tholeiitic at comparable stages and this should perhaps be taken as the essential difference. There are, however, basalts intermediate in this respect and some from Iceland provide an example. Lower alumina and higher lime in the middle stage basalts also mark out the Hebridean Tholeiitic basalts from the Alkaline, and this feature is also detectable in the Deccan and Karroo middle stage basalts. The Mauritian basalt series are close enough to the Hebridean Alkaline series to be named as such, but at the middle stage they are poorer in alumina and richer in lime than the type series.

Another result of this work is to show that, even in the better-known basalt provinces, there is still too little data for defining with precision the changes in composition during fractionation of the various magma series. It seems likely that there are significant differences in parental magma in the different petrographic provinces, and still stronger differences in the composition of the later fractions. As chemical data on the basalts become more abundant and precise it may well be that minor chemical differences will be found to characterise the various areas of basalts. Even so it is clear that many basalts will be relatively silica-rich for their fractionation stage and thus will be conveniently described as belonging to the Tholeiitic series while others will be silica-poor, and be described as belonging to an Alkaline series. It is urgently required that a limited number of provinces should be analysed into fractionation stages, and that these be accepted as types with which others may be compared. So far perhaps the Hebridean is the best available, since it covers a considerable range of stages. The Hawaiian, over its more limited range, obviously provides another useful type area. Even within the broad fields of the Plateau and Tholeiitic magma types several other type provinces (e.g., the Karroo) will probably have to be established.

Consideration of the Relationship of the Alkaline and Tholeiitic Magma Series

The Plateau magma in the Hebrides is apparently an early magma leading by fractionation to the mugearites and the trachytes. The Tholeiitic magma

series, on the other hand, does not apparently include such early-stage types, and in this respect at least it could have been developed from the Plateau magma. For the Hebridean area there is no concensus as to which magma should be regarded as the parent or what otherwise may be the relationship of the two series. Similarly in Hawaii the question whether the Tholeiitic basalts have been derived in some way from Alkaline series, or vice versa, has not been decided. The Tholeiitic basalts build the accessible parts of Mauna Loa and Kilauea, and they are reported as occurring beneath the Alkaline basalt series on the three other volcanoes in Hawaii, which show declining stage differentiates. Indeed, one analysed basalt from Hualalai, mentioned earlier (p. 225) belongs to the Tholeiitic rather than the Alkaline series. Many investigators have felt that the magma type, which builds the bulk of the vast pile forming the island of Hawaii, is Tholeiitic in character. Perhaps the reason for this belief is that the volcanoes Mauna Loa and Kilauea, which are at present actively building up, are producing Tholeiitic lavas, and by extrapolation it is thought that the whole building up of the pile from the sea-floor has been by this magma type. Also the Alkaline magma series has clearly developed during the declining stages of Hualalai, Mauna Kea, and Kohala, and the tentative inference is again that the Plateau magma and its derivative is characteristic of the declining phase, and not of the earlier building-up stage. It must, however, be realized that there is no positive evidence for the nature of the material forming the greater part of the pile, and the question of its composition is open. Judging by the accessible rocks, the Tholeiitic lavas of Hawaii are not appreciably fractionated, and they are visualized as the products of a magma pool which was in an active stage and perhaps enlarging itself by melting processes. On the other hand the Alkaline magma series, as seen in Hawaii, shows an extensive series of fractionation stages, and is presumably due to cooling and fractional crystallizing of a pool, or pools, of Plateau magma beneath the volcanoes.

There are two important ways in which the Hebridean Tertiary volcanic province differs fundamentally from Hawaii. In the first place the Hebridean province is within a continental area, the Lewisian gneisses of the north-west Highlands being demonstrably present at no great depth beneath the region. No petrological or geophysical evidence suggests that such continental sialic rocks are present in Hawaii. Among the British Tertiary volcanic rocks, granite and granophyres are abundant, but these types are absent in Hawaii. It seems likely that the occurrence of abundant acid rocks in the Hebrides is directly related to the presence of the sialic layer. The second significant difference between the two areas is that the Hebridean basalts now available for study are at or near the bottom of the lava pile, and represent the earlier stages of volcanic activity, while in Hawaii the only rocks which can be examined are the later ones, resting on 20,000 ft or more of inaccessible lavas below sea-level. The available Hawaiian story is only the last chapter, and it might look rather different if we could reach rocks belonging to the earlier ones.

When the stages of fractionation of the Hebridean Tholeiitic basalts were first considered by the method used here, it was thought possible that a clue might be provided to the extent of contamination of basalt magma by sialic crustal rocks. It seemed evident on general compositional grounds that, if basalt incorporated

a small amount of granitic rock, or such material as CLARK and WASHINGTON's average crustal rock (1924, p. 16), there would be little change in the iron-to-magnesium ratios and only a small change in the albite ratio, but that there would be a marked increase in SiO_2 and K_2O percentages. Thus it was hoped to divide the basalts of any one stage into two significantly different groups, one having high SiO_2 and K_2O due to contamination with sial and the other not. Tholeiitic basalt as here distinguished is higher in SiO_2 but not in K_2O, and its origin by simple contamination is thought unlikely. On the other hand, some lava series which are not our concern at the moment probably involve contamination at some stage.

In considering the problem of the relationship between the Tholeiitic and Plateau basalt types in Hawaii, a fundamental question is whether one type is parental, and, if so, is the Tholeiitic type derived from the Alkaline, or vice versa? POWER's view (1955) is that normal fractionation is not likely to give the saturated Tholeiitic basalts from the Plateau basalt of the Alkaline magma series, or vice versa. TILLEY's tentative view (1950, p. 44) is that the Tholeiitic magma is parental, and that it has been subjected to different conditions during fractionation to give two alternative lines of descent. This idea was originally suggested in general terms by BOWEN, on the basis of his discovery of the reaction relationship of olivine to its usual melt (BOWEN, 1928, pp. 238–9). He pointed out that, if early-separated olivine reacts with the magma, giving pyroxenes, then silica will be used up and, on fractionation, an Alkaline series of rocks might develop (for Hawaii, cf. TILLEY, 1950, p. 38). On the other hand, if early-formed olivine does not have an opportunity to react with the liquid, then more silica is left in the residual liquid, and a more silica-rich series of differentiates should result. Other suggested ways by which the trend of fractionation of basic magma may perhaps vary, depend on the early phases separating from the parent magma being markedly influenced by high pressure, or by different water content, or by different degrees of oxidation, so that the composition of the successive residual liquids is changed.

A different kind of hypothesis to account for the appearance of the two main types of basalt is one which postulates fusion of different independent crustal layers as the immediate source. Since the Plateau and Tholeiitic basalt types are both present in Hawaii as well as in the Hebrides, this view would necessitate the existence of crustal layers* corresponding to both these types in oceanic as well as continental environments. Furthermore, since preliminary consideration of some other regions shows that local varieties, or even intermediate types of the Plateau and Tholeiitic basalts, exist, this hypothesis would suggest variations in the composition of the successive crustal layers in different parts of the world.

Melting or partial melting, by local rise of the geo-isotherms or by relief of pressure, is usually accepted as the means by which magmas are produced. The story of Tertiary igneous activity in Great Britain, which is the completest yet available, may be tentatively thought of as due first to the extensive production

* Recent geophysical work by RAITT (quoted in POWERS, 1955, p. 97) now suggests a 5-km layer beneath the Pacific transmitting waves of intermediate velocity appropriate to basalt.

of an early-stage Plateau basalt magma by partial melting of a crustal layer, probably peridotitic in composition. During subsequent periods of cooling and crystallization the Plateau magma pools apparently underwent fractional crystallization with the production of rocks of the Alkaline magma series. At local centres, melting of a higher layer seems to have produced Tholeiitic lavas, and in some places the Tholeiitic magma pools underwent differentiation by fractionation as, for example, in Mull, where intermediate minor intrusions of Non-porphyritic Central type and possibly small amount of acid magma may have been produced in this way. To the writer it does not seem likely, however, that all the rocks ascribed to the Mull normal magma series are directly and wholly the product of differentiation of Tholeiitic basalt magma, and especially it does not seem likely that the bulky granitic rocks of Mull are the final product of differentiation of Tholeiitic basalt. It seems more probable that the granites and granophyres of the British Tertiary igneous province have resulted from melting of the higher, sialic layers of the area, the process of melting being activated by basic magma of Tholeiitic, or even Plateau basalt composition.

Acknowledgements—The writer is grateful to Dr. H. J. Harrington (New Zealand Geological Survey) who helped in the early stages of this work by discussion of the problems and by plotting analyses, and to Miss Dorothy Stroud, who has since carried out, with great care, the greater part of the plotting and averaging which has been required.

I also thank my colleagues Dr. L. H. Ahrens, Dr. E. A. Vincent, Dr. R. L. Oliver, Dr. G. M. Brown, and Dr. S. R. Taylor, for helpful suggestions after critical reading of the manuscript.

Appendix 1.

List of analyses of Hawaiian lavas in order of stage of fractionation, as used in constructing the albite and iron ratio plots, Figs. 2, 3, and 4

Serial number	*Fractionation stage*	*Name*	Macdonald (1949a) *Page and Number*		*Co-ordinates of points* *Ab ratio*	*Fe ratio*
1	Early α	Picrite-basalt	63	7	40·5	23·4
2		Picrite-basalt	74	1	41·2	22·6
3		Picrite-basalt	73	1	42·9	22·3
4		Olivine basalt	78	1	40·8	25·8
5	Early β	Olivine basalt	73	3	49·4	23·1
6		Picrite-basalt	63	8	49·6	24·5
7		Picrite-basalt	83	2	54·7	20·2
8		Picrite-basalt	63	3	60·6	14·9
9		Olivine (?) basalt	87	9	38·8	36·3
10		Basalt	1572*	5	44·6	33·5
11		Olivine basalt	74	5	51·6	27·3
12		Hyp.-bearing basalt	63	2	39·6	39·9
13		Olivine basalt	74	4	49·2	30·6
14		Basalt	73	8	40·4	39·6
15	Middle α	Non-porphy. ol. basalt	83	1	45·1	35·4
16		Olivine basalt	74	7	43·4	39·2
17		Olivine basalt	74	9	42·7	40·7
18		Basalt	63	9	45·8	38·5
19		Basalt	87	10	53·8	33·0
20		Hyp.-bearing basalt	63	11	46·5	40·5
21		Hyp.-bearing basalt	63	14	47·1	39·9
22		Basalt	63	10	44·0	43·0
23		Olivine basalt	87	2	49·6	39·2
24		Basalt (?)	73	6	44·3	45·0
25		Olivine basalt	74	13	46·8	43·0
26	Middle β	Olivine basalt	74	6	51·3	38·8
27		Basalt	83	5	46·2	45·0
28		Olivine basalt	74	10	47·7	43·2
29		Olivine basalt	63	1	56·9	34·8
30		Basalt	63	4	46·1	45·6
31		Basalt	1572*	4	43·9	48·2
32		Basalt	1572*	2	45·2	47·0
33		Olivine basalt	83	6	46·8	45·0
34		Basalt	63	12	53·2	40·3
35		Olivine basalt	63	13	52·6	41·5
36		Olivine basalt	83	4	48·1	48·0
37		Basalt	78	5	54·0	42·8
38		Oligoclase andesite	87	1	63·2	34·2
39	Late α	Olivine basalt	87	5	58·7	44·4
40		Olivine basalt	78	2	66·0	34·3
41		Andesite	83	11	62·2	48·1
42		Andesite	83	7	60·3	53·7
43		Andesite	83	9	62·5	52·4
44		Andesine andesite	87	4	68·6	43·9
45	Late β	Oligoclase andesite	87	7	64·9	53·6
46		Andesite	83	10	70·7	44·1
47		Olivine basalt	87	8	70·2	50·8
48		Oligoclase andesite	87	12	75·1	55·8
49		Oligoclase andesite	87	11	79·3	55·5
50	Late Differentiates	Trachyte	78	8	92·0	7·5
51		Trachyte obsidian	78	9	100·0	78·7

Note: Localities are indicated by the page references; p. 63 indicates Mauna Loa; pp. 73 and 74 Kilauea; p. 78 Hualalai; p. 83 Mauna Kea; p. 87 Kohala. * Macdonald (1949b) Nos. 4 and 5 Mauna Loa, No. 2 Kilauea.

Appendix 2.

List of lava analyses of the Hebridean Tertiary igneous province in order of stage of fractionation as used in constructing the albite and iron ratio plot, Fig. 5

Serial No.	*Fractionation stage*	*Name*	*Locality*	*Reference*	*Co-ordinates of points*	
					Ab ratio	*Fe ratio*
1	Early α	Olivine basalt (Lower Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 1.	34·7	26·7
2		Olivine basalt (Upper Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 5.	34·5	27·7
3		Olivine basalt (Upper Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 6.	37·2	25·0
4		Olivine basalt (Lower Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 3.	34·4	29·7
5		Basalt (Porphyritic Central type)	Mull	Mull Memoir (1924) p. 24, No. III (Surv. Anal. 261).	35·5	29·9
6		Basalt (Porphyritic Central type)	Mull	Mull Memoir (1924) p. 24, No. V (Surv. Anal. 252)	35·6	30·4
7		Fine-grained basalt	Skye	KING (1953) p. 365, No. 1.	31·9	33·3
8		Basalt (Porphyritic Central type)	Mull	Mull Memoir (1924) p. 24, No. IV (Surv. Anal. 259).	28·8	36·7
9		Olivine dolerite (Plateau magma)	Skye	HARKER (1904) p. 248, No. II (Surv. Anal. 285).	36·0	33·7
10	Early β	Olivine basalt (Plateau magma)	Morven, Mull	Mull Memoir (1924) p. 15, No. III (Surv. Anal. 281).	41·3	31·8
11		Olivine basalt (Lower Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 2.	39·2	33·8
12		Basalt	Skye	KING (1953) p. 365, No. 2.	39·2	35·2
13		Olivine basalt (Plateau magma)	Skye	HARKER (1904) p. 31, (Surv. Anal. 267).	43·0	33·2
14		Olivine basalt (Upper Lava Series)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 4.	44·9	33·4
15		Tholeiitic basalt (Middle Lava Series) (No. 6 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. VIII.	41·9	36·3
16		Basalt	Mull	NOCKOLDS and ALLEN (1954) p. 254, No. 1.	43·0	36·3
17	Middle α	Tholeiitic basalt	Staffa	HOLMES (1936) p. 90.	43·9	39·6
18		Tholeiitic basalt (Middle Lava Series) (No. 3 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. V.	48·7	36·8
19		Tholeiitic basalt (Middle Lava Series) (No. 5 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. VII.	52·8	33·5
20		Tholeiitic basalt (Middle Lava Series) (No. 7 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. X.	47·2	40·1
21		Tholeiitic basalt (Middle Lava Series) (No. 4 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. VI.	50·9	36·4
22		Tholeiitic basalt (Middle Lava Series) (No. 1 flow-Colonnade)	N. Ireland	HOLMES (1936) p. 91.	46·3	41·9
23	Middle β	Olivine basalt (Plateau magma)	Morven, Mull	Mull Memoir (1924) p. 15, No. II (Surv. Anal. 282).	45·2	45·4
24		Porphyritic basalt	Skye	KING (1953) p. 365, No. 3.	40·2	50·1
25		Tholeiitic basalt	N. Ireland	TOMKEIEFF (1940) p. 110, No. 6.	48·2	43·4
26		Basalt (Non-porphyritic Central type)	Mull	Mull Memoir (1924) p. 17, No. III (Surv. Anal. 247).	50·0	44·7
27		Olivine basalt (Plateau magma)	Rhum	HARKER (1908) p. 57, No. I (Surv. Anal. 269).	50·4	44·8
28		Tholeiitic basalt (Middle Lava Series) (No. 6 flow-central part)	N. Ireland	PATTERSON (1955) p. 107, Table VIII, No. IX.	54·6	41·2
29		Tholeiitic basalt (Middle Lava Series) (No. 2 flow-Colonnade)	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 8.	50·5	46·7
30	Late α	Olivine dolerite	Skye	HARKER (1904) p. 248, No. I (Surv. Anal. 274).	54·2	50·4
31		Porphyritic olivine dolerite (Mugearite)	Skye	HARKER (1904) p. 263, No. I (Surv. Anal. 245).	55·0	51·0
32		Basalt (Middle Lava Series)(No. 2 flow—Entablature)	N. Ireland	TOMKEIEFF (1940) p. 110, Table IV, No. 7.	55·5	54·3
33		Basalt (Non-porphyritic Central type)	Mull	Mull Memoir (1924) p. 17, No. IV (Surv. Anal. 244)	59·2	50·8
34		Doleritic Mugearite (Alkaline magma series)	Rhum	HARKER (1908) p. 130, No. III (Surv. Anal. 299).	63·3	49·8
35		Olivine dolerite	Canna	HARKER (1908) p. 125, No. I (Surv. Anal. 250).	64·2	53·5
36	Late β	Basalt (Non-porphyritic Central type)	Mull	Mull Memoir (1924) p. 17, No. V (Surv. Anal. 241).	61·0	64·0
37		Doleritic Mugearite (Alkaline magma series)	Canna	HARKER (1908) p. 130, No. II (Surv. Anal. 303).	71·3	46·3
38		Mugearite-basalt	Skye	NOCKOLDS and ALLEN (1954) p. 254, No. 4.	67·1	57·6
39		Mugearite (Alkaline magma series)	Skye	HARKER (1904) p. 263, No. II (Surv. Anal. 305).	77·3	56·1
40	Late Differentiates	Rhyolite	N. Ireland	HOLMES (1936) p. 94.	64·3	75·0
41		Quartz-trachyte (Upper Lava Series)	N. Ireland	PATTERSON (1951) p. 278, Table I, No. A.	81·3	82·0
42		Quartz-trachyte	N. Ireland	PATTERSON (1951) p. 278, Table I, No. B.	85·5	51·5
43		Mugearite	Skye	NOCKOLDS and ALLEN (1954) p. 254, No. 9.	88·3	69·7
44		Trachyte	Skye	NOCKOLDS and ALLEN (1954) p. 254, No. 11.	89·5	31·2
45		Mugearite (Alkaline magma series)	Mull	Mull Memoir (1924) p. 27, No. I (Surv. Anal. 298).	90·8	74·0
46		Obsidian	N. Ireland	PATTERSON (1951) p. 286, Table 1, No. 12.	92·5	73·5
47		Rhyolite	N. Ireland	PATTERSON (1951) p. 286, Table I, No. 13.	65·3	100·0
48		Trachyte (Alkaline mama series)	Mull	Mull Memoir (1924) p. 27, No. IV, (Surv. Anal. 88)	98·6	72·2

Note: The Surv. Anal. number refers to the number of the analysis in "Chemical analyses of igneous rocks, metamorphic rocks and minerals," GUPPY and THOMAS (1931).

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Etude statistique sur les caractères géochimiques des eaux douces au Japon—I

Aspect général de la distribution de fréquence des concentrations des composants dans les eaux douces, et essai d'estimation de la qualité la plus commune des eaux douces au Japon

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(*Received* 31 *October* 1955)

Abstract—Frequency distributions of the concentrations of several constituents in 627 samples of the fresh waters in Japan have been examined. Ca, Mg, SO_4, and SiO_2 are lognormally distributed, or nearly so, and as a result arithmetic mean and geometric mean calculations are accurately related. Cl is not lognormally distributed. These results indicate that lognormality is common in nature.

Introduction. La méthode statistique est en particulier efficace pour la recherche géochimique dans l'hydrosphère. La nature géochimique de l'eau naturelle évolue toujours. Pour en saisir les caractéristiques dynamiques, il faut adopter nécessairement la méthode statistique. Pourtant cette méthode n'était pas familière aux chercheurs hydrogéochimiques. Nous pensons pouvoir éclaircir beaucoup de caractéristiques inconnues de l'eau naturelle en appliquant la méthode statistique.

Eaux examinées. Dans le but de trouver des sources d'eau pour chaudières, l'Institut Téchnologique du Chemin de fer a examiné en 1940 les teneurs de l'eau douce en divers composants le long du chemin de fer dans tout le Japon. Ces données analytiques chimiques (J.S.P.S.R., 1942) conviennent assez bien pour notre recherche actuelle.

La forme de distribution de fréquence des concentrations des composants dans les eaux douces au Japon. Le Tableau 1 montre les fréquences des concentrations des composants dans les eaux douces. Un simple coup d'oeil indique que la distribution des fréquences ne se forme pas suivant l'allure normale. Nous avons examiné sur un graphique de probabilité la forme de distribution (Figs. 1, 2, 3, 4, 5, et 6) et obtenue des résultats très intéressants.

(i) Pour les composants tels que calcium, magnésium, sulfate et silicium, la distribution des fréquences du logarithme des concentrations (et non pas des fréquences des concentrations propres) prend à peu près l'allure normale.

(ii) Quant au chlorure et au résidu d'évaporation (Ré), l'aspect est un peu différent. La forme de distribution du chlorure dans l'eau de rivière, ainsi que dans l'eau souterraine, paraît assez irrégulière. La forme de distribution du résidu d'évaporation est à peu près lognormale seulement dans l'eau souterraine. L'irrégularité se trouvant dans le chlorure paraît provenir de l'échantillonnage imparfait de l'eau à analyser. Nous avons déjà reconnu que l'activité humaine donne beaucoup de chlorures à l'eau naturelle, particulièrement au Japon

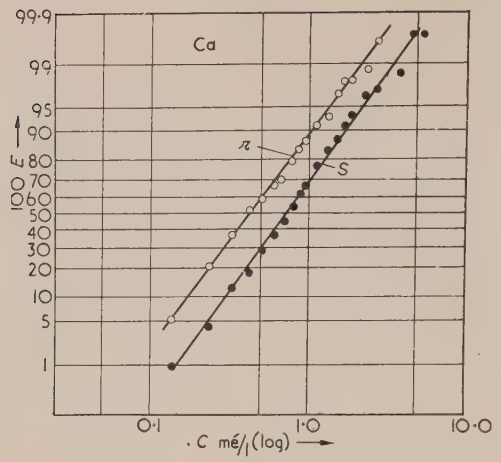

FIG. 1. Distribution du calcium

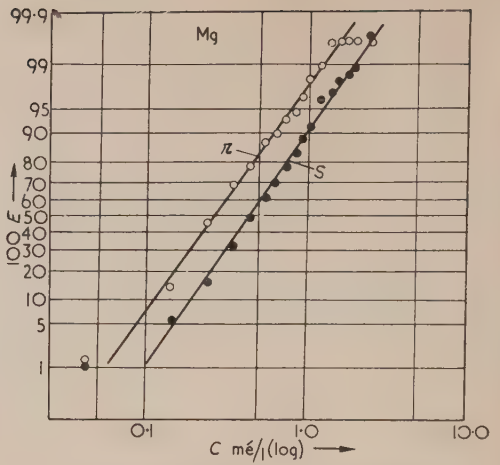

FIG. 2. Distribution du magnésium

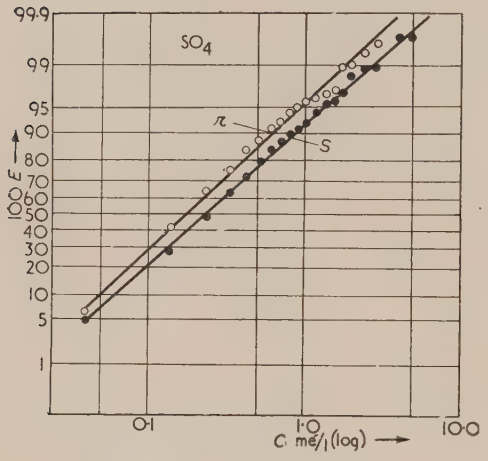

FIG. 3. Distribution du sulfate

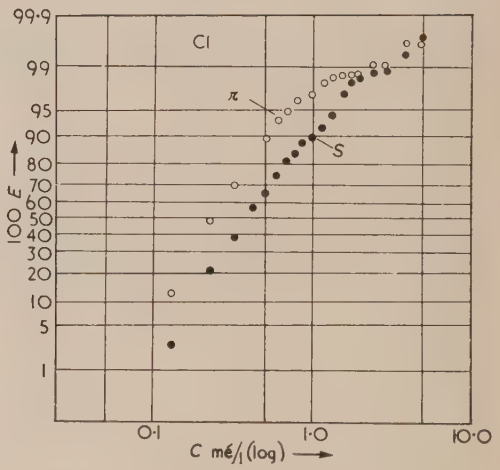

FIG. 4. Distribution du chlorure

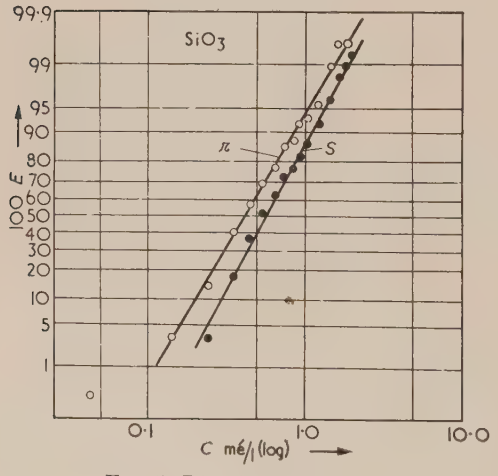

FIG. 5. Distribution du silicium

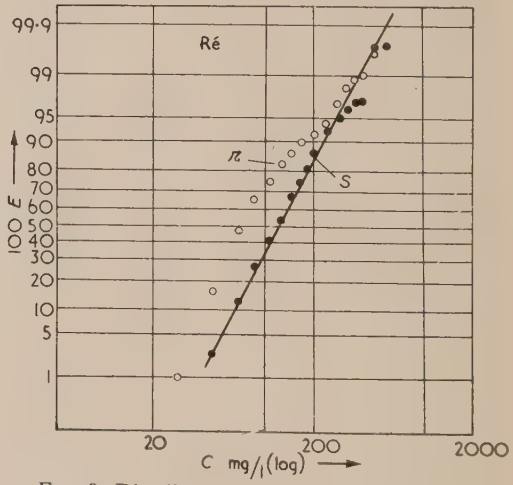

FIG. 6. Distribution du résidu d'évaporation

Dans les Figures 1, 2, 3, 4, 5 et 6.

c: concentrations des composants, mé/l ou mg/l

$$100E = 100x \int_{-\infty}^{x} Z\,dx, \quad Z \equiv \frac{1}{\sqrt{2x}}\, e^{-\frac{x^2}{2}}, \quad x = \log C$$

r: eau de rivière

s: eau souterraine.

Tableau 1 (a)

Concentration mé/l	Eau souterraine									
	Ca		Mg		SO_4		Cl		SiO_3*	
	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)
0,00 ~ 0,04	0	0	4	1,2	17	5,2	0	0	0	0
0,05 ~ 0,14	3	0,9	15	5,8	76	28,6	9	2,8	0	0
0,15 ~ 0,24	10	4,0	32	15,7	63	48,0	62	21,8	10	3,1
0,25 ~ 0,34	28	12,6	58	33,5	51	63,7	57	39,4	49	18,2
0,35 ~ 0,44	19	18,5	53	49,8	32	73,5	55	56,3	60	36,6
0,45 ~ 0,54	32	28,3	39	61,8	21	80,0	31	65,8	51	52,3
0,55 ~ 0,64	28	36,9	31	71,4	16	84,9	31	75,4	36	63,4
0,65 ~ 0,74	30	46,1	21	77,8	9	87,6	19	81,1	30	72,6
0,75 ~ 0,84	30	55,4	22	84,5	6	89,5	12	84,9	16	77,5
0,85 ~ 0,94	26	63,4	13	88,5	6	91,4	10	88,0	15	82,1
0,95 ~ 1,04	15	68,0	10	91,6	3	92,1	5	89,5	16	87,0
1,05 ~ 1,24	30	77,2	16	96,5	8	94,7	9	92,2	17	92,2
1,25 ~ 1,44	19	83,1	2	97,3	4	96,0	6	94,1	14	96,5
1,45 ~ 1,64	15	87,7	3	98,1	1	96,3	10	97,3	6	98,5
1,65 ~ 1,84	12	91,4	1	98,5	3	97,3	3	98,1	2	99,0
1,85 ~ 2,04	7	93,5	1	98,8	5	98,8	1	98,5	1	99,4
2,05 ~ 2,54	10	96,5	3	99,7	1	99,0	1	98,8	2	100,0
2,55 ~ 3,04	2	97,3	1	100,0	0	99,0	0	98,8	0	
3,05 ~ 4,04	4	98,5	0		2	99,7	2	99,4	0	
4,05 ~ 5,04	4	99,7	0		0	99,7	1	99,7	0	
5,05 ~ 6,04	0	99,7	0		1	100,0	1	100,0	0	
6,05 ~ 7,04	1	100,0	0		0		0		0	
Total	325	100,0	325	100,0	325	100,0	325	100,0	325	100,0

* Nous avons calculé le silicium comme SiO_3^{2-} malgré que l'état du silicium dans l'eau ne soit pas déterminé.

Tableau 1 (b)

Concentration mé/l	Eau de rivière									
	Ca		Mg		SO_4		Cl		SiO_3*	
	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)
0,00 ~ 0,04	0	0	4	1,3	19	6,3	0	0	1	0,3
0,05 ~ 0,14	15	5,0	36	13,2	105	41,1	37	12,3	8	3,0
0,15 ~ 0,24	46	20,2	98	45,6	70	64,2	108	48,0	30	12,9
0,25 ~ 0,34	52	37,4	72	69,5	35	75,9	63	68,8	78	38,7
0,35 ~ 0,44	44	52,0	29	79,1	25	84,1	45	83,7	53	56,3
0,45 ~ 0,54	19	58,3	24	87,1	11	87,8	17	89,4	38	68,8
0,55 ~ 0,64	27	67,2	9	90,0	11	91,4	12	93,4	25	77,2
0,65 ~ 0,74	23	69,9	10	93,4	5	93,0	5	95,0	25	85,4
0,75 ~ 0,84	13	79,2	4	94,6	5	94,7	4	96,4	9	87,5
0,85 ~ 0,94	15	84,1	6	96,7	2	95,3	2	97,0	11	92,1
0,95 ~ 1,04	8	86,7	5	98,4	2	96,0	0	97,0	4	93,4
1,05 ~ 1,24	14	91,4	2	99,0	1	96,4	3	98,0	7	95,7
1,25 ~ 1,44	6	93,4	2	99,6	2	97,0	2	98,5	10	99,0
1,45 ~ 1,64	10	96,7	0	99,6	1	97,3	0	98,5	2	99,6
1,65 ~ 1,84	4	98,0	0	99,6	5	99,0	0	98,5	0	99,6
1,85 ~ 2,04	0	98,0	0	99,6	0	99,0	0	98,5	1	100,0
2,05 ~ 2,54	2	98,7	0	99,6	1	99,4	1	99,0	0	
2,55 ~ 3,04	3	99,6	1	100,0	1	99,6	0	99,0	0	
3,05 ~ 4,04	1	100,0	0		1	100,0	2	99,6	0	
4,05 ~ 5,04	0		0		0		0	99,6	0	
5,05 ~ 6,04	0		0		0		1	100,0	0	
6,05 ~ 7,04	0		0		0		0		0	
Total	302	100,0	302	100,0	302	100,0	302	100,0	302	100,0

* Nous avons calculé le silicium comme SiO_3^{2-} malgré que l'état du silicium dans l'eau ne soit pas déterminé.

Tableau 1 (c)

Concentration mg/l	Résidu d'évaporation			
	Eau de rivière		Eau souterraine	
	fréquence (nombre)	total (%)	fréquence (nombre)	total (%)
0 ~ 10	0	0	0	0
11 ~ 30	3	1,0	0	0
31 ~ 50	45	15,9	9	2,8
51 ~ 70	95	47,3	35	13,5
71 ~ 90	60	67,2	47	28,0
91 ~ 110	29	76,8	46	42,1
111 ~ 130	20	83,4	41	54,8
131 ~ 150	12	87,4	27	69,2
151 ~ 170	11	91,0	23	76,3
171 ~ 190	4	92,4	19	82,1
191 ~ 210	5	94,0	17	87,5
211 ~ 250	9	97,0	20	93,5
251 ~ 290	4	98,4	5	95,0
291 ~ 330	1	98,7	4	96,3
331 ~ 370	1	99,0	2	97,0
371 ~ 410	2	99,7	1	97,2
411 ~ 510	1	100,0	8	99,7
511 ~ 610	0		0	99,7
611 ~ 811	0		1	100,0
	302	100,0	325	100,0

(Hanya, 1951). L'échantillonnage de l'eau examinée pour chaudières est nécessairement plus fréquent dans le domaine où l'activité humaine est animée, que dans le lieu où n'existe pas le chemin de fer. Donc il semble que la forme de distribution de fréquence du chlorure dans cet échantillonnage, ainsi que celle du résidu d'évaporation qui contient du chlorure, soit déviée de celle du Japon tout entier. La déviation est plus évidente dans l'eau de rivière que dans l'eau souterraine qui a, en général, plus de salinité que celle de rivière.

Estimation de la qualité commune de l'eau douce au Japon. Suivant le fait que les fréquences des concentrations des composants dans les eaux douces sont lognormales, nous pouvons évaluer stochastiquement la concentration moyenne arithmétique ainsi que la concentration moyenne géométrique.

(i) Mode de calcul de la valeur moyenne. En prenant C_i comme teneur en élément dans l'eau, nous avons évalué stochastiquement ($\alpha = 0.05$, α: niveau de significance) la valeur moyenne arithmétique de $\log C_i$ ($=\overline{\log C}$). La valeur de $10^{\overline{\log C}}$ correspond à celle de la moyenne géométrique de C_i ($= Gm$). Ensuite nous avons calculé stochastiquement ($\alpha = 0{,}1$) la variance (u^2) de $\log C_i$.

$$u^2 = \frac{1}{N-1} \sum_{i=1}^{N} (\log C_i - \overline{\log C})^2$$

où
$$\begin{cases} N \text{ est le nombre d'échantillons,} \\ \overline{\log C} = \dfrac{1}{N} \sum_{i=1}^{N} \log C_i \end{cases}$$

Nous pouvons estimer ($\alpha < 0{,}1$) la valeur moyenne arithmétique de C_i ($\equiv Am$), en appliquant l'équation suivante (AHRENS, 1954b).

$$\log \frac{Am}{Gm} = 1{,}153u^2$$

(ii) *Résultat.* Le Tableau 2 montre le résultat de notre estimation.

Tableau 2

Composant		Gm ($\alpha = 0{,}05$)	Am ($\alpha < 0{,}1$)	u^2 ($\alpha = 0{,}1$)
Ca (mé/l)	r*	0,42 ~ 0,48	0,52 ~ 0,65	0,086 ~ 0,117
	s*	0,72 ~ 0,83	0,88 ~ 1,10	0,077 ~ 0,105
Mg (mé/l)	r	0,25 ~ 0,29	0,31 ~ 0,39	0,083 ~ 0,107
	s	0,42 ~ 0,48	0,50 ~ 0,60	0,063 ~ 0,085
SO_4 (mé/l)	r	0,16 ~ 0,20	0,24 ~ 0,35	0,156 ~ 0,213
	s	0,21 ~ 0,26	0,34 ~ 0,51	0,186 ~ 0,251
Cl (mé/l)	r	—	—	—
	s	—	—	—
SiO_2 (mé/l)	r	0,39 ~ 0,44	0,41 ~ 0,53	0,049 ~ 0,068
	s	0,54 ~ 0,59	0,61 ~ 0,70	0,048 ~ 0,064
Ré (mg/l)	r	—	—	—
	s	104 ~ 126	126 ~ 146	0,040 ~ 0,054

* r: eau de rivière; s: eau souterraine.

Discussion. Nous avons mis en évidence pour la première fois la distribution lognormale de fréquence des concentrations dans les eaux douces au Japon (HANYA et SAWADA, 1953). En ce qui concerne les roches, L. H. AHRENS avait mis en évidence la même loi de distribution lognormale de fréquence des teneurs de quelques éléments traces dans quelques espèces de roches (AHRENS, 1954a).

Cela suggère que la loi de distribution lognormale est valable non seulement dans les eaux mais encore dans les roches, et comme AHRENS a déjà clairement indiqué, elle deviendra une des lois les plus importantes de la géochimie.

Quant à la qualité de l'eau, nous avons mis en évidence que la concentration la plus commune des éléments est un peu plus grande que celle de la moyenne arithmétique. Mais la différence est petite, et la caractéristique qualitative indiquée jusqu'à présent pour la concentration moyenne arithmétique s'applique encore à celle de la moyenne géométrique.

A nos grands regrets, dans l'état actuel des recherches, il nous est encore impossible d'éclaircir le mécanisme de la distribution lognormale. Mais au point de vue de la géochimie descriptive, cette loi sera très importante pour notre recherche.

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The melting of asteroids and the origin of meteorites

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(*Received* 21 *October* 1955)

Abstract—The radioactive heating of spherical bodies is discussed, and it is shown that it is possible to investigate the melting of asteroids quantitatively as well as qualitatively. The mathematical solution of the problem embodies a parameter which makes it relatively easy to take into account both the effect of varying size and of conductivity. A number of different models are considered, which allow for both a cold and a hot origin and for different concentrations of radioactivity. The results are compared with the data available from studies of meteorites, and a number of general conclusions are drawn.

Introduction

An important question which arises in a discussion of the origin of meteorites and of the solar system is whether asteroidal-type objects could have melted due to their own radioactivity within a reasonable time after the formation of the solar system. G. P. Kuiper (1954) and H. C. Urey (1955), in two important recent papers, have discussed this matter, and have come to somewhat different conclusions. Kuiper states that all spheres larger than about 100 km in diameter would have melted, at least close to their centres, during the first 10^9 years of their history. Urey feels, on the other hand, that the heat produced by uranium, thorium, and potassium would not be sufficient, and that some other effects, such as the decay of the short-lived isotope Al^{27}, must have been present for melting to have occurred.

It is necessary for any thorough investigation of this problem to consider the effects of varying the size of the asteroid, the thermal conductivity of its material, and the concentrations of the various radioactive substances heating it. To attempt to produce numerical results might therefore seem foolhardy, but it is shown below that the mathematical solutions used can be put in a form which makes the effect of varying size and conductivity very easy to ascertain, and for which different concentrations of radioactivity can be tried without prohibitive labour. Thus the melting of asteroids can be discussed quantitatively as well as qualitatively.

Method of Calculation

The changes in temperature produced by radioactive heating within a sphere have been discussed by the authors in several papers and in a forthcoming book (Jacobs and Allan, 1954; Allan, 1955; Allan, in press; Jacobs, in press). This was with special reference to the earth; for an asteroid a simplification may be introduced, in that the radioactivity may be taken as distributed uniformly throughout it, which reduces the complexity of the mathematical solution considerably. Even if radioactivity has been concentrated towards the surface of an asteroid, the central and average temperature may be calculated with little error from the homogeneous solution using the (low) concentrations found in the bulk of the asteroid.

Consider a homogeneous sphere of density ρ, specific heat c, and thermal conductivity K, and with uniform radioactivity throughout, the decay-constant and initial rate of heat production of which are λ and H_0 respectively. If the initial temperature is zero and the surface

remains at zero temperature, the temperature θ at distance r from the centre and at time t is given by

$$\frac{\theta}{J} = \left\{ \frac{a \sin \sqrt{\frac{\lambda}{k}}\, r}{r \sin \sqrt{\frac{\lambda}{k}}\, a} - 1 \right\} \frac{e^{-\lambda t}}{\lambda} - \frac{2a^3}{\pi^3 k r} \sum_{m=1}^{\infty} e^{-\frac{m^2\pi^2 k t}{a^2}} \cdot \sin \frac{m\pi r}{a} \cdot \frac{(-1)^m}{m\left(\frac{a^2\lambda}{\pi^2 k} - m^2\right)} \tag{1}$$

$$= \frac{2a^3}{\pi^3 k r} \sum_{m=1}^{\infty} \left(e^{-\lambda t} - e^{-\frac{m^2\pi^2 k t}{a^2}} \right) \sin \frac{m\pi r}{a} \cdot \frac{(-1)^m}{m\left(\frac{a^2\lambda}{\pi^2 k} - m^2\right)} \tag{2}$$

where J has been written for $H_0/\rho c$ and k for $K/\rho c$.

The quantities of interest in this discussion are the central temperature θ_c, i.e., the temperature when $r = 0$, and the average temperature $\bar{\theta}$ defined by

$$\bar{\theta} = \frac{3}{a^3} \int_0^a r^2 \theta \, dr \tag{3}$$

Table 1. Values of central temperature functions (θ_c/J)
(units 10^9 yr)

t (10^9 yr) \ λ (10^{-9} yr^{-1})	0·972	0·550	0·154	0·0499
	$\nu = 0{\cdot}5 \times 10^{-9}$			
0·5	0·396	0·437	0·481	0·494
1	0·634	0·764	0·921	0·970
2	0·765	1·079	1·567	1·743
3	0·636	1·047	1·862	2·207
4	0·455	0·866	1·918	2·439
5	0·293	0·660	1·840	2·527
	$\nu = 10^{-9}$			
0·5	0·393	0·434	0·478	0·491
1	0·571	0·695	0·848	0·894
2	0·486	0·737	1·144	1·294
3	0·285	0·551	1·137	1·397
4	0·145	0·364	1·033	1·390
5	0·069	0·227	0·907	1·345
	$\nu = 10^{-8}$			
0·5	0·113	0·133	0·155	0·161
1	0·070	0·101	0·144	0·157
2	0·026	0·059	0·123	0·150
3	0·010	0·034	0·106	0·142
4	0·004	0·019	0·090	0·136
5	0·001	0·011	0·078	0·129

Note: The values for $\nu = 0$ are identical with those in Table 2, q.v.

Define a parameter ν as $\pi^2 k/a^2$, then these quantities may be written as

$$\frac{\theta_c}{J} = \left\{ \frac{\pi\sqrt{\frac{\lambda}{\nu}}}{\sin \pi\sqrt{\frac{\lambda}{\nu}}} - 1 \right\} \frac{e^{-\lambda t}}{\lambda} - \frac{2}{\nu} \sum_{m=1}^{\infty} e^{-m^2\nu t} \frac{(-1)^m}{\left(\frac{\lambda}{\nu} - m^2\right)} \tag{4}$$

$$= \frac{2}{\nu} \sum_{m=1}^{\infty} (e^{-\lambda t} - e^{-m^2\nu t}) \frac{(-1)^m}{\left(\frac{\lambda}{\nu} - m^2\right)} \tag{5}$$

and

$$\frac{\bar{\theta}}{J} = \left\{ \frac{3\nu}{\pi^2\lambda} - \frac{3}{\pi}\sqrt{\frac{\nu}{\lambda}} \cot \pi\sqrt{\frac{\lambda}{\nu}} - 1 \right\} \frac{e^{-\lambda t}}{\lambda} + \frac{6}{\nu\pi^2} \cdot \sum_{m=1}^{\infty} \frac{e^{-m^2\nu t}}{m^2\left(\frac{\lambda}{\nu} - m^2\right)} \tag{6}$$

$$= \frac{6}{\nu\pi^2} \sum_{m=1}^{\infty} \frac{e^{-m^2\nu t} - e^{-\lambda t}}{m^2\left(\frac{\lambda}{\nu} - m^2\right)} \tag{7}$$

Table 2. Values of average temperature functions ($\bar{\theta}/J$)
(units 10^9 yr)

t (10^9 yr) \ λ (10^{-9} yr^{-1})	0·972	0·550	0·154	0·0499	t (10^9 yr) \ λ (10^{-9} yr^{-1})	0·972	0·550	0·154	0·0499
	$\nu = 0$					$\nu = 10^{-10}$			
0·5	0·396	0·437	0·481	0·494	0·5	0·333	0·368	0·405	0·418
1	0·640	0·769	0·927	0·976	1	0·492	0·598	0·727	0·768
2	0·882	1·213	1·721	1·903	2	0·584	0·826	1·206	1·345
3	0·973	1·469	2·403	2·786	3	0·561	0·888	1·532	1·804
4	1·008	1·617	2·986	3·626	4	0·509	0·871	1·748	2·174
5	1·021	1·702	3·487	4·425	5	0·455	0·800	1·882	2·472
	$\nu = 10^{-12}$					$\nu = 0{\cdot}5 \times 10^{-9}$			
0·5	0·390	0·429	0·479	0·486	0·5	0·263	0·295	0·326	0·335
1	0·624	0·750	0·906	0·960	1	0·341	0·421	0·521	0·552
2	0·835	1·174	1·665	1·842	2	0·312	0·468	0·722	0·817
3	0·926	1·403	2·305	2·676	3	0·227	0·403	0·782	0·949
4	0·950	1·530	2·845	3·460	4	0·152	0·313	0·769	1·007
5	0·953	1·597	3·300	4·198	5	0·097	0·229	0·719	1·021
	$\nu = 10^{-11}$					$\nu = 10^{-9}$			
0·5	0·375	0·403	0·457	0·469	0·5	0·218	0·244	0·272	0·280
1	0·590	0·705	0·861	0·906	1	0·250	0·314	0·395	0·421
2	0·780	1·079	1·547	1·714	2	0·178	0·286	0·469	0·538
3	0·829	1·266	2·102	2·448	3	0·098	0·203	0·500	0·563
4	0·830	1·352	2·551	3·118	4	0·048	0·131	0·403	0·554
5	0·815	1·338	2·915	3·732	5	0·022	0·081	0·352	0·534

The behaviour of these functions is illustrated in Figs. 1 and 2, for the case $\lambda = 0{\cdot}550 \times 10^{-9}\,\mathrm{yr}^{-1}$, the decay-constant of potassium-40. Tables 1 and 2 list the calculated values of θ_c/J and $\bar{\theta}/J$ for different values of λ.

The temperature produced by a number of radioactive substances may be found by adding

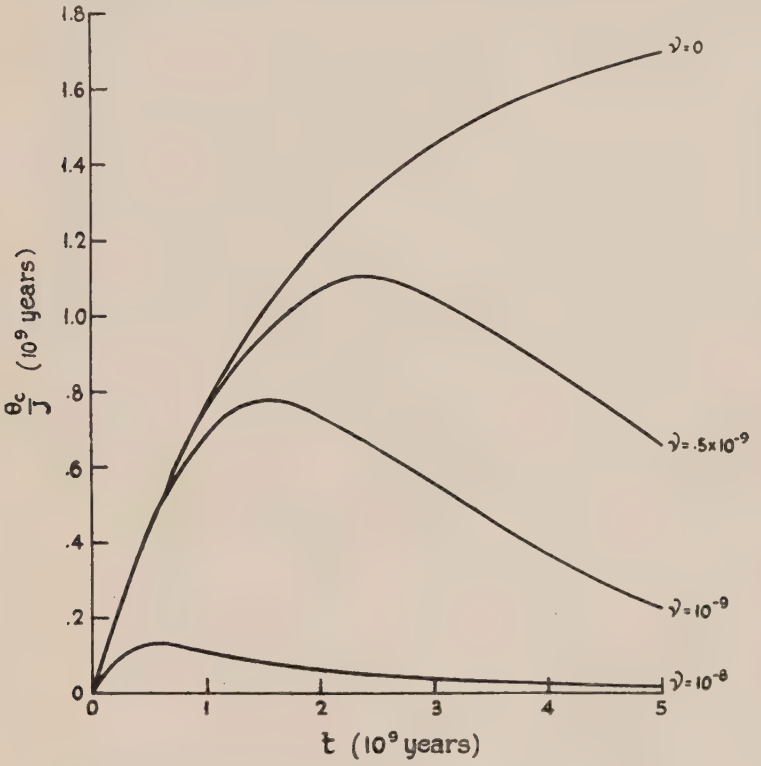

Fig. 1. Central temperature function ($\lambda = 0{\cdot}55 \times 10^{-9}\,\mathrm{yr}^{-1}$).

the contributions from each individual substance, as given by the above formulae. Thus, for a given set of values $J_1, J_2, J_3, \ldots$, the central and average temperatures are given by

$$T_c(\nu, t) = \sum_i J_i \theta_c(\lambda_i, \nu, t) \tag{8}$$

and

$$\overline{T}(\nu, t) = \sum_i J_i \bar{\theta}(\lambda_i, \nu, t) \tag{9}$$

From graphs of these functions the time required to raise the central and average temperatures of a given sphere to the melting-point can be estimated. The time required to melt a certain fraction of the sphere, say a volume V_1, can also be found if it is assumed that the surface-heat flow of the sphere remains the same as it would if the sphere were solid. (This should be true for a fair range of values of V_1, since melting will start from the centre.) If this is so, then

$$\begin{aligned}\text{total heat produced} &= \text{heat required to melt } V_1 + \text{heat lost from the surface} \\ &= \rho L V_1 + \text{heat lost from the surface},\end{aligned}$$

where L is the latent heat.

But if V is the total volume, the heat lost from the surface = total heat produced = $\rho c V \times$ (change in average temperature). Hence, $\rho L V_1 = \rho c V \times$ (change in average temperature), and thus the time required to melt V_1 can be found from the graph of average temperature.

The above formulae give the temperature changes due to radioactive heating alone. The effect of the sphere possessing an initial temperature above its surroundings is easy to ascertain: if the sphere is initially at temperature T_0, and the surroundings at zero, then after time t the central and average temperatures are given by

$$T_c/T_0 = 2\sum_{m=1}^{\infty}(-1)^{m+1}\,e^{-m^2\nu t} \tag{10}$$

and

$$\overline{T}/T_0 = \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{e^{-m^2\nu t}}{m^2} \tag{11}$$

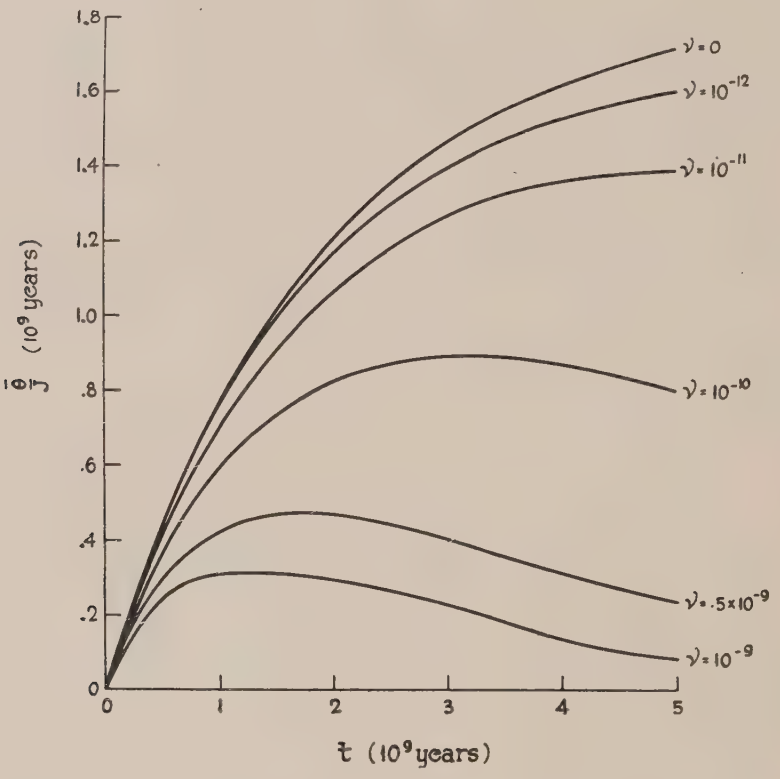

Fig. 2. Average temperature function ($\lambda = 0{\cdot}55 \times 10^{-9}\ \mathrm{yr}^{-1}$).

Tables 3 and 4 list values of these functions, most of them being taken from Appendix H of *Heat Conduction* by Ingersoll and Zobel (McGraw-Hill). The combined effect of radioactive heating and cooling from an initial temperature is found by adding the two sets of results.

Data Used

The only radioactive substances whose heating effects need be considered are U^{235}, U^{238}, Th^{232}, and K^{40}. The values for their decay-constants used in the present calculations are:

U^{235}	$0{\cdot}972 \times 10^{-9}\ \mathrm{yr}^{-1}$
K^{40}	$0{\cdot}550 \times 10^{-9}\ \mathrm{yr}^{-1}$
U^{238}	$0{\cdot}154 \times 10^{-9}\ \mathrm{yr}^{-1}$
Th^{232}	$0{\cdot}0499 \times 10^{-9}\ \mathrm{yr}^{-1}$

Table 3. Central temperature T_c/T_0 (non-radioactive sphere)

t (10^9 yr) \ v (yr^{-1})	0	$0{\cdot}5 \times 10^{-9}$	10^{-9}	10^{-8}
0·5	1·0000	0·9996	0·9639	0·0135
1	1·0000	0·9639	0·6994	0·0001
2	1·0000	0·6994	0·2700	0·0000
3	1·0000	0·4413	0·0996	0·0000
4	1·0000	0·2700	0·0366	0·0000
5	1·0000	0·1641	0·0135	0·0000

Table 4. Average temperature $\overline{T}/T_0$ (non-radioactive sphere)

t (10^9 yr) \ v (yr^{-1})	0	10^{-12}	10^{-11}	10^{-10}	$0{\cdot}5 \times 10^{-9}$	10^{-9}
0·5	1·0000	0·9761	0·9253	0·7743	0·5372	0·3901
1	1·0000	0·9662	0·8956	0·6897	0·3901	0·2264
2	1·0000	0·9524	0·8537	0·5789	0·2264	0·0823
3	1·0000	0·9419	0·8231	0·5010	0·1360	0·0303
4	1·0000	0·9331	0·7967	0·4401	0·0823	0·0111
5	1·0000	0·9253	0·7743	0·3901	0·0499	0·0041

The radioactive concentrations are not, of course, well known. Furthermore, to a given set of present values correspond any number of sets of values, depending on the time chosen in the past for the start of the heating process; i.e., if the present rate of heat production by a radioactive substance is H, and $H/\rho c$ be denoted by J_0, then the value to be used in the calculations is $J = J_0 e^{\lambda t_0}$ where t_0 is the time-interval since the start of the heating process. The authors have been content for the present to take four sets of values of J_0. Two have been taken from Urey's (1955b) article—the first set is actually derived from the concentrations reported for a chondritic meteorite by Paneth's group, and Urey chose the second by dividing the first by 3·2, a figure found by assuming the radioactivity in the earth to be in the same proportion as in the meteorites and comparing the total heat produced by the radioactivity with the surface heat flow. The third set was found by averaging the values used by the authors in their earth models (Allan, 1955; Jacobs, in press). The fourth set is obtained from the concentration found in dunite, a terrestrial rock which may be representative of the earth's mantle. Similar values (actually lower by about one-half) have been reported for the uranium content of pallasitic meteorites. These four distributions together cover a fair range of possibilities, since the first represents about the highest values likely, lower values than the third would not be expected

for "cosmic matter," and the fourth should be of the order of magnitude likely for differentiated material. These sets of values of J_0 are listed in Table 5.

One choice of a date for the heating process to begin will of course be the supposed age of the solar system. The age of the earth has lately been reviewed

Table 5. Values of J_0 used in different models (units 10^{-7} °C/yr)

Model number	U^{235}	K^{40}	U^{238}	Th^{232}
(1)	0·14	0·98	3·11	2·77
(2)	0·044	0·31	0·97	0·87
(3)	0·038	0·15	0·80	0·81
(4)	0·023	0·013	0·47	0·48

by several authors (Patterson *et al.*, 1955; Russell and Allan, in press; Shillibeer and Russell, 1955), and there seems to be general agreement that it is about $4\frac{1}{2}$ thousand million years. This is in agreement with present estimates for the age of the universe and the oldest stars. Furthermore, several meteorites have recently been dated with fair accuracy as about $4{\cdot}5 \times 10^9$ yr old (Wasserburg and Hayden, 1955; Patterson, 1955). Hence, one value taken for t_0 has been $4{\cdot}5 \times 10^9$ yr. Since all these estimates involve considerable uncertainty. a second value of $5{\cdot}5 \times 10^9$ years has also been considered; it is unlikely that the solar system had its origin any earlier than this.

Table 6. Values of J used in calculations (units 10^{-6} °C/yr)

Distribution	U^{235}	K^{40}	U^{238}	Th^{232}
A	1·11	1·16	0·622	0·347
B	2·94	2·02	0·725	0·364
C	0·348	0·364	0·195	0·109
D	0·921	0·633	0·227	0·114
E	0·302	0·178	0·160	0·100
F	0·797	0·309	0·187	0·107
G	0·183	0·0154	0·0940	0·0601
H	0·482	0·0268	0·110	0·0632
I	0·0424	0·00677	0·0746	0·0558

Table 6 lists the values of J used in the calculations. Distributions A and B are obtained from the first set of the values of J_0 given in Table 5, with t_0 taken as $4{\cdot}5$ and $5{\cdot}5 \times 10^9$ yr respectively. Similarly, C and D are from the second set, E and F from the third, and G and H from the fourth. I is also obtained from the fourth, with $t_0 = 3 \times 10^9$ yr. For convenience of calculation, these values are listed to three figures, though of course no such inherent accuracy is claimed for them.

Interpretation of the results requires a knowledge of the melting-point of the materials of the body considered. The melting-point of silicates is usually taken as around 1000° to 1500°C. 1300°C is used in most of the discussion of this paper. The melting-point of pure iron is 1535°C. The effect of pressure is to raise these melting-points. For example, the melting-point of the silicaceous mantle of the earth at the core-mantle boundary (at which the pressure is about $1{\cdot}5 \times 10^6$ atm) has been estimated by various authors as from 4000° to 6500°C, and SIMON (1953) has calculated the melting-point of iron at comparable pressures to be nearly 4000°C. These facts must be borne in mind when considering bodies large enough to have developed high internal pressures. However, these effects can be neglected for quite a large range of sizes. Even for a body as large as the moon (diameter 3500 km, central pressure about 5×10^4 atm), the rise in melting temperature at the centre would be less than 400°, and the increase for a body of diameter 2000 km would be only about 140°. Thus it seems safe to use the above melting-point values uncorrected for pressure effects for bodies up to at least 2000 km in diameter.

The heat of fusion of iron is about 65 cal/gm. Since its specific heat is about 0·6 cal/gm°C, the correction LV_1/cV mentioned in the previous section would be about 50°C. (This would allow for the heat required to melt iron of half the volume of the body considered.) For silicaceous material with $L = 100$ cal/gm and specific heat about 0·2 cal/gm°C, LV_1/cV is about 250°C. 200°C has therefore been adopted as a reasonable figure to use in making the correction for the heat of fusion. This correction may seem small, but because of the manner in which it is applied (to the *average* temperature graphs) it occasionally becomes considerable as the results described in the next section show.

Finally, to assign a value of the parameter ν to any particular body, it is necessary to know the diffusivity of its material as well as its size. Two different types of material have been considered: first, the powdery type of material of which the asteroids would originally be formed according to the accretion theory of the origin of the solar system (KUIPER, 1951, 1953), and secondly the rock-like material of which stony meteorites are made. The diffusivity of the former may be estimated (though with uncertain justification) by observing that a number of small-grained or powdered materials (such as dry quartz sand, dry soil, and insulating material like ground cork) have diffusivities of from 0·002 to 0·004 cm²/sec. If this analogy is correct, then 10^{-3} cm²/sec may be taken as the order of magnitude of the diffusivity for the powdery material. A representative value for the diffusivity of the rocky material is 0·01 cm²/sec.

Results and Their Interpretation

There seem at present to be two main lines of thought on the origin and history of meteorites. It is generally agreed that they mostly originated as fragments of an asteroidal body (or bodies) which before it was broken up by collision had undergone a heating process of some kind which caused differentiation of its material, with the formation of an iron core, and the concentration of radioactivity towards the surface. Thus iron meteorites are considered to have come from the central regions of such an asteroid, and chondritic meteorites, now

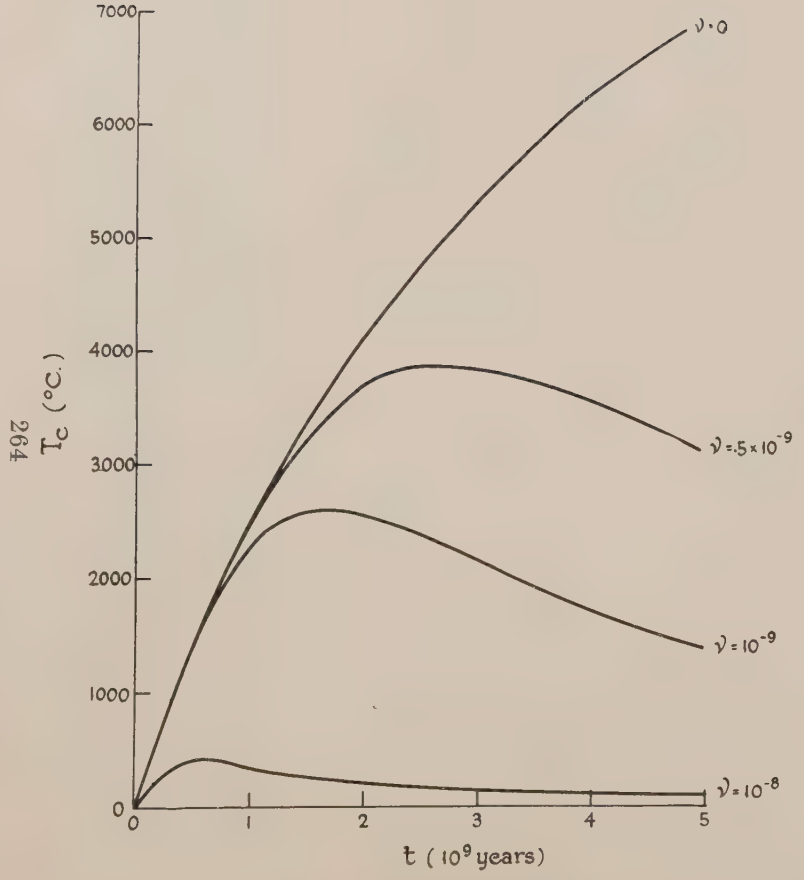

Fig. 3. Central temperature—distribution A.

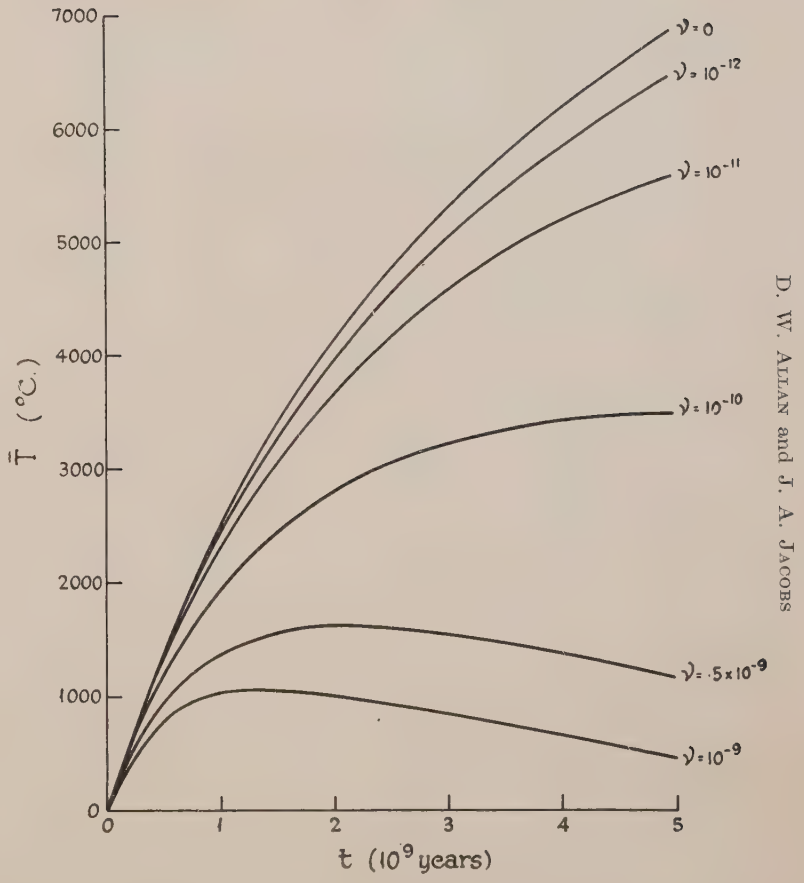

Fig. 4. Average temperature—distribution A.

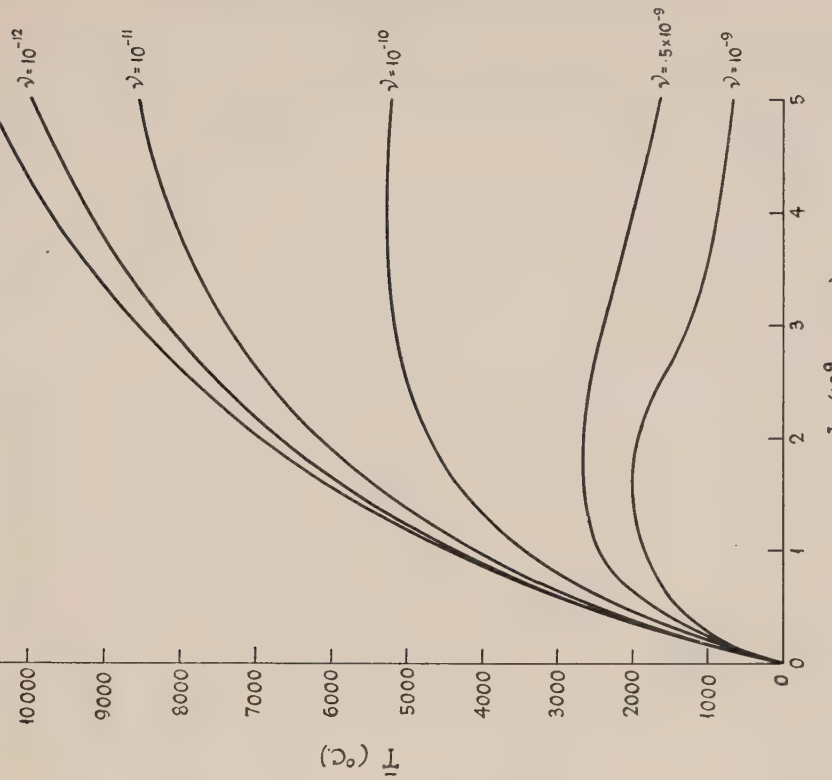

Fig. 6. Average temperature—distribution *B*.

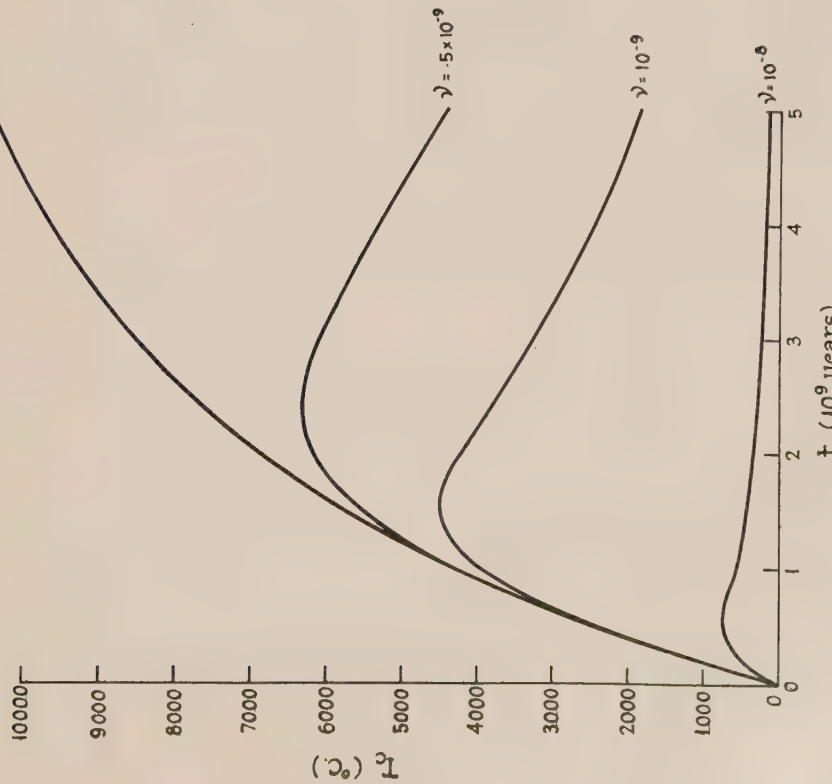

Fig. 5. Central temperature—distribution *B*.

known to have higher-than-average radioactivity, from near its surface. What is in dispute is the nature of the heating process which produced this differentiation. The two opposing views are: either the asteroids began hot, whether because of the presence of short-lived isotopes at the time of their formation or for some other reason, or they were formed by accretion, were relatively cold, and were heated up to the melting-point over a long period of time by their own radioactivity. The methods of this paper enable one, given the initial state of an asteroid, to trace its subsequent thermal history in a general manner and throw some light on this question. The following possible initial conditions have therefore been investigated:

(1) The asteroids began hot, and with low concentrations of radioactivity. Distributions G and H, plus an initial temperature of 1300°C, are used. (The diffusivity used in interpreting the results will be that for rock.)

(2) They were formed at low temperatures, by accretion, with "average cosmic" concentrations of radioactivity and diffusivities comparable to those of insulators. Distributions C and D, and E and F, are used. The results for C and D may be obtained from those for A and B (Figs. 3 to 6) by remembering that the temperature scale must be multiplied by 1/3·2.

(3) They were formed at low temperatures, but with the relatively high concentrations of radioactivity of distributions A and B (i.e., the concentrations actually found in chondritic meteorites). Again, $k = 0{\cdot}001$.

(4) Asteroids which had melted after origins (2) or (3) then solidified and continued with low concentrations of radioactivity. t_0 is taken as 3×10^9 yr in this case, and from this and line 4 of Table 5, distribution I is obtained. Distribution I, plus initial temperature 1300°C, is then used for this model.

In interpreting the results obtained under these conditions, it is convenient to have a table of the values of ν corresponding to different sizes of asteroid and the two values considered for k. These are given in Table 7. The following observations are of interest:

Table 7. Values of ν

Diameter (km)	Rocky material ($k = 0{\cdot}01$ cm^2/sec)	Powdery material ($k = 0{\cdot}001$ cm^2/sec)
10	10^{-5}	10^{-6}
50	$0{\cdot}5 \times 10^{-6}$	$0{\cdot}5 \times 10^{-7}$
100	10^{-7}	10^{-8}
200	$0{\cdot}3 \times 10^{-7}$	$0{\cdot}3 \times 10^{-8}$
300	10^{-8}	10^{-9}
400	$0{\cdot}8 \times 10^{-8}$	$0{\cdot}8 \times 10^{-9}$
500	$0{\cdot}5 \times 10^{-8}$	$0{\cdot}5 \times 10^{-9}$
600	$0{\cdot}3 \times 10^{-8}$	$0{\cdot}3 \times 10^{-9}$
800	$0{\cdot}2 \times 10^{-8}$	$0{\cdot}2 \times 10^{-9}$
1000	10^{-9}	10^{-10}
1500	$0{\cdot}6 \times 10^{-9}$	$0{\cdot}6 \times 10^{-10}$
2000	$0{\cdot}3 \times 10^{-9}$	$0{\cdot}3 \times 10^{-10}$

Bodies with origin (1) would cool in a time-span of 4 or 5 thousand million years to average temperatures of one or two hundred degrees if their diameters were from 1000 to 2000 km. Smaller bodies would cool more rapidly, and any with diameters less than 500 km would have interior temperatures of a few tens of degrees within 10^9 yr. The central temperature is more critically dependent on the diameter. Bodies larger than about 1500 km would heat up rather than cool at the centre; bodies smaller than about 500 km would have central temperatures of a few tens of degrees within 10^9 years. These general remarks are true whether t_0 is 4·5 or 5·5 thousand million years, i.e., for either of distributions G or H. The diagrams corresponding to G only are given (Figs. 9 and 10).

In the case of model (2), for melting at the centre to *begin*, the asteroid's diameter would have to be larger than about 500 km for distribution C, 300 km for D, 700 km for E, and 500 km for F, and the time required to reach the melting-point would be 2, 1, 3, and $1\frac{1}{2}$ thousand million years respectively. For substantial melting, i.e., melting of about one-half the volume, the diameter would have to be larger than about 1000, 700, 1500, and 1000 km (listing the results in the same order as before) and the time required would be approximately 1 to 2, $\frac{1}{2}$, 1 to 2, and $\frac{1}{2}$ thousand million years. Thus the total time required would be 3 to 4 thousand million years for distribution C, $1\frac{1}{2}$ for D, 4 or 5 for E, and 2 for F. As explained above, the results for distributions C and D may be found from Figs. 3, 4, 5, and 6. Those for E are given as Figs. 7 and 8.

With the high concentrations of model (3), central melting would occur for bodies as small as 300 km (distribution A) or 200 km (distribution B), and within 300 or 200 million years. Substantial melting would take place for objects of this size or larger, and would require only 200 million years or less. Within less than 500 million years, then, bodies larger than about 300 km would have been melted by their own radioactivity. Figs. 3 to 6 cover this case.

The results for model (4) are very similar to those for model (1) (distributions G and H), differing only in that cooling is a little more rapid. Again, the bodies would have to be smaller than about 1500 km in diameter to cool at the centre at all, and would have to be between 500 and 1000 km in diameter to reach temperatures of between 300° and 600° within 1 or 2 thousand million years. Because of the similarity of the results for distributions G, H, and I, the graphs for G only are given (in Figs. 9 and 10).

The evaluation of these results requires a review of the data available from studies of meteorites. As mentioned before, Wasserburg and Hayden (1955) have dated two meteorites by the potassium-argon method as about $4\frac{1}{2}$ thousand million years old, and Patterson (1955) gives three Pb^{207}/Pb^{206} ages of about the same value. Patterson also states that iron meteorites are probably about the same age. Gerling and Pavlova (1951) reported lower ages (about 3×10^9 yr) by the potassium-argon method, and Thomson and Mayne (1955) found two meteorites to be between 3 and 4×10^9 yr old, and one less than 2×10^9 yr. However, Urey (1955a) has suggested that Gerling and Pavlova's potassium analyses may be somewhat high, which would bring their ages into agreement with Wasserburg's, whilst the ages of the two older meteorites of Thomson and Mayne are increased to 4×10^9 yr if they are calculated using the same branching

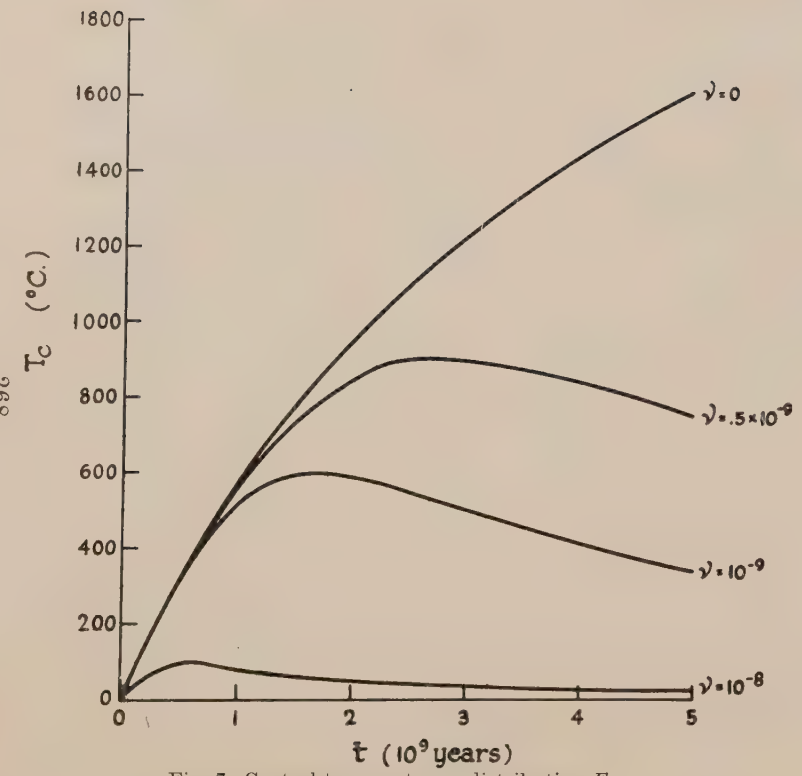

Fig. 7. Central temperature—distribution *E*.

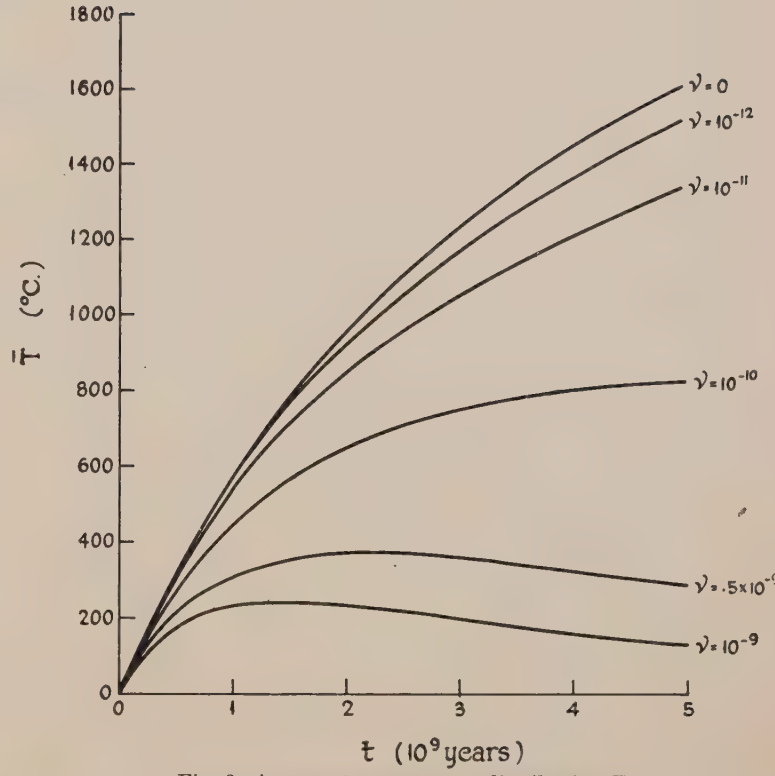

Fig. 8. Average temperature—distribution *E*.

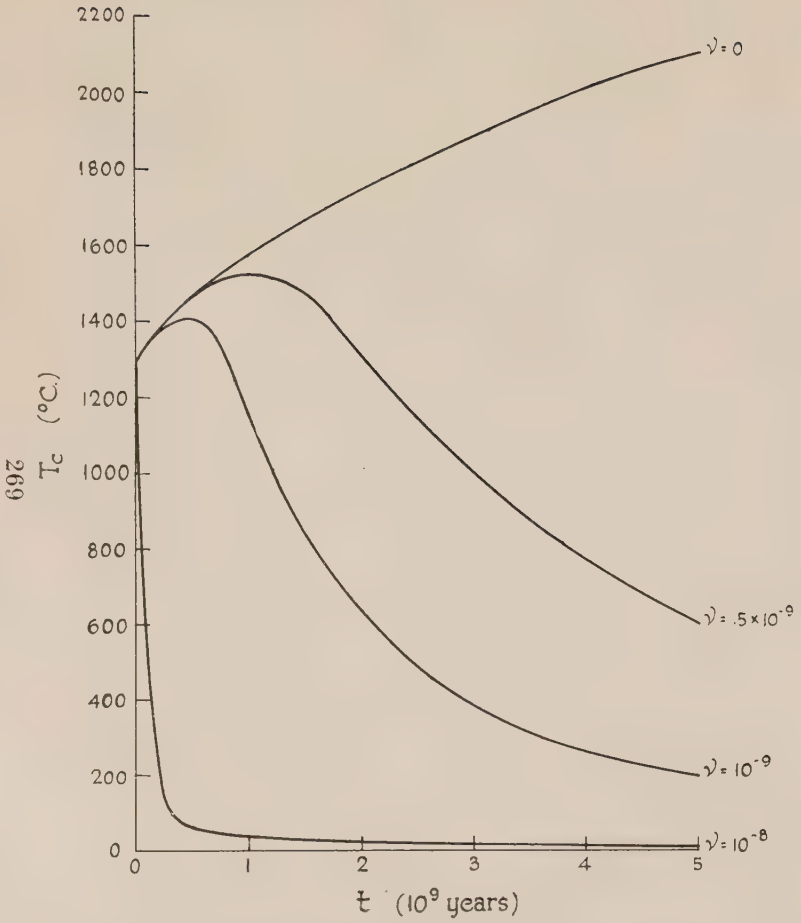

Fig. 9. Central temperature—distribution G + initial temperature.

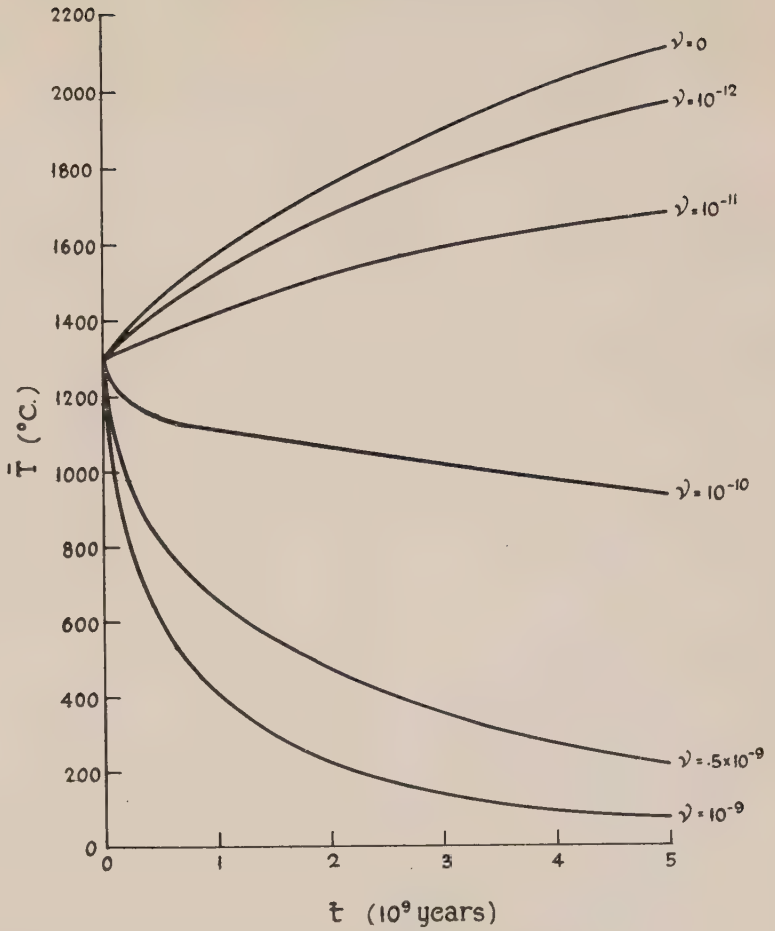

Fig. 10. Average temperature—distribution G + initial temperature.

ratio as Wasserburg did. On the whole, then, the evidence available seems to favour an age of over 4×10^9 yr for stony meteorites. There is definite disagreement on the ages of the iron meteorites. Reasbeck and Mayne (1955) believe the ages of the irons to be an order of magnitude lower (viz., 2 or 3 $\times$ 10^8 yr) than the stones, and offer as an explanation a planetary origin, the planet having been disrupted soon after the iron phase solidified, i.e., a relatively short time ago. Patterson, as mentioned above, prefers the view that the irons are about the same age as the stones, and Urey has recently (1955a) given an account of why he mistrusts the helium ages.

Metallurgical evidence as to the origin of the irons has been summed up very thoroughly by Uhlig in two papers (1954, 1955). He states that the Widmanstätten pattern of octahedrites formed under conditions of high pressure (of the order of 10^5 atm), that the octahedrites must have been slowly cooled from high temperatures to temperatures of about 300°C, and that Neumann bands are evidence that the meteorites formed by fragmentation of a larger body which had cooled to less than about 600°C.

It is discouraging to observe that none of the possible histories examined in the present paper fit the above evidence completely. For example, the central portions of the asteroids (from which the irons must have originated) could not have cooled slowly to temperatures of between 300° and 600°C, as Uhlig requires, unless the diameter of the asteriod was about 1000 km, and the central pressure would then be an order of magnitude or more less than he suggests. Again, if the iron core had solidified less than 10^9 years ago, as Reasbeck and Mayne believe, it could not have cooled to temperatures of less than 600°C. The best that can be done, then, is to state which of the possible histories for the asteriods fit most of the evidence, and hope that later work will resolve these contradictions.

An asteroid which began hot, as in model (1), would have cooled slowly to central temperatures of between 300° and 600°C if its diameter was about 1000 km. The central pressures would not then be high (4×10^3 atm). A small portion of the core might have remelted, but the core would certainly be solid within 10^9 yr (for $t_0 = 4{\cdot}5 \times 10^9$ yr) or 2×10^9 yr (for $t_0 = 5{\cdot}5 \times 10^9$ yr). Indeed, since the efficient differentiation produced by a liquid origin would have left the core with the very low radioactive concentrations characteristic of iron meteorites (about one-quarter of those used for distributions G and H), it is unlikely that there was any remelting, and age determinations should give the same results for iron and stone meteorites. This history would thus fit the potassium-argon age determinations, and Patterson's ideas on the age of irons, and would agree with Uhlig's conclusions as to temperatures, but would seem to disagree with the helium-age results and with Uhlig's requirement of high-pressures.

The case of a cold origin, as considered in models (2) and (3), is more complex. First of all, if t_0 is $4{\cdot}5 \times 10^9$ yr, the time required for melting, given the "average" concentrations of C and E, would be rather large (between 3 and 5 thousand million years), and the bodies would have to be nearly 1500 km in radius, which would rule out their centres cooling to below 600°C in the time available before the disruption which formed the meteorites. Furthermore, the very old ages for the stony meteorites are then hard to understand. This sequence of events,

although it could explain the helium ages for irons, therefore seems unlikely. If one is prepared to accept the high concentrations of distribution A, the situation is much more favourable. Asteroids of 300-km diameter or larger would melt in a reasonable time (less than 500 million years), and their subsequent history would then be the same as for the hot origin already discussed, e.g., 1000 km again would be their likely size. However, it is difficult to see how such high-average concentrations could occur.

For $t_0 = 5{\cdot}5 \times 10^9$ yr (i.e., distributions B, D, and F) origins of the type considered in models (2) and (3) both seem feasible. The high concentrations B again would give satisfactory results and the lower values of D and F would still serve to melt the asteroids within reasonable times ($1\frac{1}{2}$ to 2 thousand million years), and would not require over-large diameters. The ages expected for the stones and irons would be about 5×10^9 yr for distribution B and 4×10^9 yr or a little lower for distributions D and F, which are respectively a little higher and lower than one would like, but not to any drastic extent. A possible course of events which would fit in with Urey's (1955b) belief that the age of the chondritic meteorites actually represents the time at which they were formed by the shattering of an asteroidal body, not just the time of solidification of the parent body, is that a body of planetary dimensions which had been heated as above was disrupted about 4 thousand million years ago, yielding both small fragments like the chondrites and bodies of larger dimensions (say 1000 km), later collisions among which were responsible for such meteorites as irons and pallasites. The history of these latter bodies would be similar to that already discussed for the case of a hot origin. Again, whether these bodies originated in this complicated manner, or were of 1000-km dimensions from the start, as Kuiper's theory (1953) would suggest, the evidence against such a history would be the helium ages and the pressure values.

Conclusions

To make any dogmatic conclusions from the results discussed above would be most unwise, in view of the uncertainty of the data used and the approximate methods employed. For example, the value used for the conductivity of powdered material might well be an order of magnitude too large, and this would change a number of details in the above discussion (the value used for the conductivity of rock is not likely to be wrong by this amount). Further, the model of a homogeneous sphere heating uniformly to a definite melting-point is a very simplified one; a reading of Urey's paper (1955b) gives a good idea of what a complexity of processes may actually have operated. Nevertheless, the authors feel that the methods of this paper should give general results that are largely correct, so long as one does not attempt to draw too detailed conclusions, e.g., from differences of tens rather than hundreds of degrees.

In conclusion, the following results seem to deserve emphasis:

(1) A hot origin for the asteroids leads to a reasonable thermal history, whether the time of origin t_0 was 4·5 or 5·5 thousand million years ago.

(2) An origin by cold accretion and subsequent radioactive heating would be feasible for $t_0 = 5{\cdot}5$ thousand million years, or if the concentration of the radioactive substances were higher than is at present thought reasonable.

(3) In both cases, the asteroids from which the meteorites originated were probably about 1000 km in diameter, in agreement with Kuiper's calculations (1953).

(4) There may be a contradiction between the pressure and temperature requirements deduced from metallurgical studies, and the helium ages for iron meteorites are hard to reconcile with other data.

Acknowledgements—One of the authors (D. W. Allan) was assisted while writing this paper by a National Research Council of Canada fellowship.

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Note added in proof—

Since completing the above paper, the authors have had the benefit of correspondence with G. P. Kuiper, H. H. Uhlig, and H. C. Urey. Kuiper suggests that a value of 10^{-4} is a better estimate for the thermal conductivity of the outer layers of the accreted material than the value 10^{-3}, his reason being that the thermal conductivity of the surface material of the moon is as low as 3×10^{-6}. The effect of using this lower value is that in models (2) and (3) the minimum diameter quoted would be reduced to one-half or one-third the value obtained. Thus asteroids as small as about 300 km in diameter could have melted appreciably, due to their own radioactivity, if Kuiper's value of the conductivity is correct.

Uhlig has considered the problem of how a small body of about 1000 km in diameter, which size (as shown above) fits the thermal data, can give rise to a core pressure of 10^5 atmospheres, and he has suggested a model which satisfies these apparently conflicting requirements. Urey agrees with an observation by Kuiper that the heating which produced the silicate minerals and chondrites occurred before $4{\cdot}5 \times 10^9$ years ago and that no heating since then is of interest as far as they are concerned. He remarks that the real problem is "what heated the meteorites before they were agglomerated?", and reiterates his belief that radioactive heating by K, U, and Th would be insufficient.

Geochimica et Cosmochimica Acta, 1956, Vol. 9, pp. 273 to 278. Pergamon Press Ltd., London

The Sc abundance minimum in chondrites and the neutron excess of principal isotopes

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(*Received* 6 *January* 1956)

Abstract—Conspicuous abundance minima in chondrites at $Z = 21$ (Sc), $Z = 22$ (Ti), and possibly $Z = 31$ (Ga) may be correlated with discontinuities in the neutron-excess variation of principal isotopes of the elements. Some of these discontinuities are clearly related to well-established magic numbers (20 and 82, for example), but others are not.

Introduction

It will be recalled that estimates of the cosmic abundances of the elements decrease fairly regularly with Z or A. Within the trend, the greatest individual fluctuations occur over the light-mass range up to say $Z = \sim 30$. Considering even Z and odd Z elements separately, four features are conspicuous over the range $Z = \sim 10$ to $Z = \sim 30$; namely, for even Z, a marked abundance minimum at $Z = 22$ (Ti) and maximum at $Z = 26$ (Fe); and for odd Z elements, a marked abundance minimum at $Z = 21$ (Sc) and maximum at $Z = 25$ (Mn) (Fig. 1). A further very notable feature over this range is the close similarity of the even Z and odd Z abundance curves (see, for example, Fig. 9.1 of Rankama, 1954). Considering even and odd Z elements together, two of the above features are particularly prominent—the Fe abundance "peak" and Sc abundance "valley." The Fe abundance maximum is often discussed and emphasized (see, for example, Alpher and Herman, 1953), whereas little attention has been paid to the Sc minimum. A communication (Pinson, Ahrens, and Franck, 1953) on the abundances of Li, Sc, Sr, Ba, and Zr in chondrites, noted that the conspicuous low abundance of Sc might bear some relationship to the neutron excess (N–Z) of the principal (most abundant)* isotopes of the odd Z elements; this observation and some related aspects are discussed in the present paper.

Sources of Abundance Data

The abundance estimates of Urey (1952) and those of Pinson, Ahrens, and Franck (1953) and Sandell (1955), for Sc and Ga respectively, will be used here, unless stated otherwise. With the exception of the recent Ga estimate, these values are the same as those adopted by Rankama (1954) and used to construct his Fig. 9.1.

Before proceeding to the main discussion, we should note that Suess and Urey (1955) have quite recently published another set of cosmic abundance estimates: as in most previous sets, many of the values are primarily based on the analyses of chondrites, but the cosmic abundances which these authors

* This ranges from 100% for some elements to as low as 27·13% for Nd^{142}, the most abundant isotope of neodymium (see discussion concerning the significance of the neutron number 82).

recommend are not necessarily the original analyses. They remind us that, although fairly smooth relationships between chondrite abundances and Z (or A) exist, there are several irregularities, varying in degree; and SUESS and UREY suggest that a better abundance estimate may sometimes be obtained by smoothing out irregularities; other considerations are also taken into account when recommending a value. For the purpose of the present paper, the raw data have

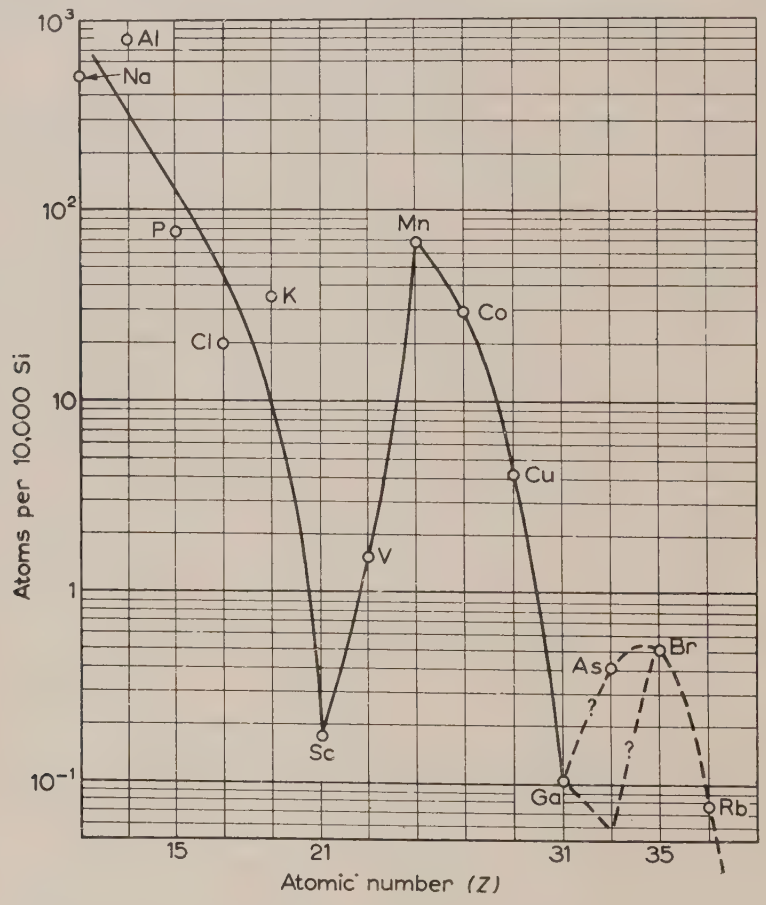

Fig. 1. Variation of abundance with Z, over range $Z = 11$ to $Z = 39$ (odd Z elements only).

been used. An attempt will not be made here to compare the merits of each revised estimate with that of the actual determination (in any case, the differences are often not significant for this discussion), but two examples, that of Sc and its relationship to Ga, and that of As, will be considered because of their particular interest for the discussion which follows. In common with most elements thus far thoroughly examined, the abundances of Sc (PINSON, AHRENS, and FRANCK, 1953) and Ga (SANDELL, 1955) are extremely uniformly distributed in chondrites. SUESS and UREY suggest that the measured abundance of Sc in chondrites (Sc = 20, when Si = 10,000) is low, and they recommend a value of 48 for the

cosmic abundance of this element.* As evidence supporting the need for this revision, they state that their attention has been drawn (Russell, private communication) to the fact that the lines of scandium are much more intense in the sun's spectrum than are those of Ga, despite the greater intrinsic intensity of the lines of Ga, whose abundance is apparently roughly similar in magnitude to Sc. Such a comparison might be misleading. It is true that the Ga spectrum is much brighter than that of Sc in a low-energy source (flame and d.c. arc, for example), but the reverse might hold in a high-energy source such as the sun, and in this paper the original abundance estimate of 20 will be retained in place of value of 48. It should be added that use of the higher value does not remove the Sc abundance minimum on Fig. 1, but merely makes it less conspicuous.

The abundance of As in meteorites has recently been re-determined by Onishi and Sandell (1955), who obtain an average (2·2 p.p.m.) in chondrites which is decidedly less than the earlier values (Noddack, 1934) in meteorites. It seems unlikely that analytical error is significant in these recent analyses, but the large spread of As values (0·8 to 4·0 p.p.m.) in the chondrites is quite unusual, and contrasts very sharply with the great majority of elements in chondrites. This could be caused in part by the fact that As is strongly concentrated in the metal phase, and variable metal content would presumably bring about As fluctuation. This, however, does not hold for Ga, which is also enriched in the metal phase of meteorites but which nevertheless is present at very uniform concentrations. There is the possibility that As variation could be due to variable loss by volatilization, in which case the value of 2·2 p.p.m. would be an underestimate. There is the question also of whether chondrites alone should be used for arriving at an abundance estimate for an element such as As, and whether some weight should not be given to the iron meteorites; inclusion of some iron weighting would presumably elevate the estimated abundance. There is evidently considerable uncertainty about the precise abundance of As, and when discussing its abundance relative to that of Ga, cognizance will be taken of the above observations.

General Discussion

When considering the possible significance of any correlation between the Sc abundance minimum and the N–Z variation of the principal isotopes of odd Z elements, it is instructive also to consider even Z elements; accordingly, Fig. 2 relates N–Z to Z in both even and odd Z elements. For odd Z elements there is rarely difficulty in distinguishing the principal isotope, because never more than two are present: but for even Z elements, difficulty may be found above $Z = \sim 30$, because of the presence of many isotopes; and as a result, Fig. 2 is confined to light elements. For odd Z elements alone, Fig. 3 is given to show variation of N–Z with Z throughout the whole range of Z.

After oxygen ($Z = 8$), N–Z remains uniform in the principal isotopes of both odd (N–$Z = 1$) and even (N–$Z = 0$) elements up to $Z = 20$, after which N–Z

* *Note added in proof*—These comments are based on typescript copy of the Suess and Urey paper kindly made available to me through the courtesy of Professor Urey. The final version, now just appeared (*Revs. Mod. Phys.* (1956) **28**, 53) is altered in some parts, including the discussion on the Sc-Ga abundances; their revised value for Sc abundance is 28.

increases by one step of 4 in the principal isotopes of even Z elements and two steps of 2 in the principal isotopes of odd Z elements. Sc ($Z = 21$) and Ti ($Z = 22$), the elements with conspicuously low abundance, follow immediately after the N–Z discontinuity at $Z = 20$. $Z = 20$ and $N = 20$ are favoured or magic numbers (see below) indicative perhaps of shell closure, and it is of interest to note that the abundance of Ca is not at a *conspicuous* maximum; rather, it seems that the most marked features resulting from this development are the Sc-Ti minima.

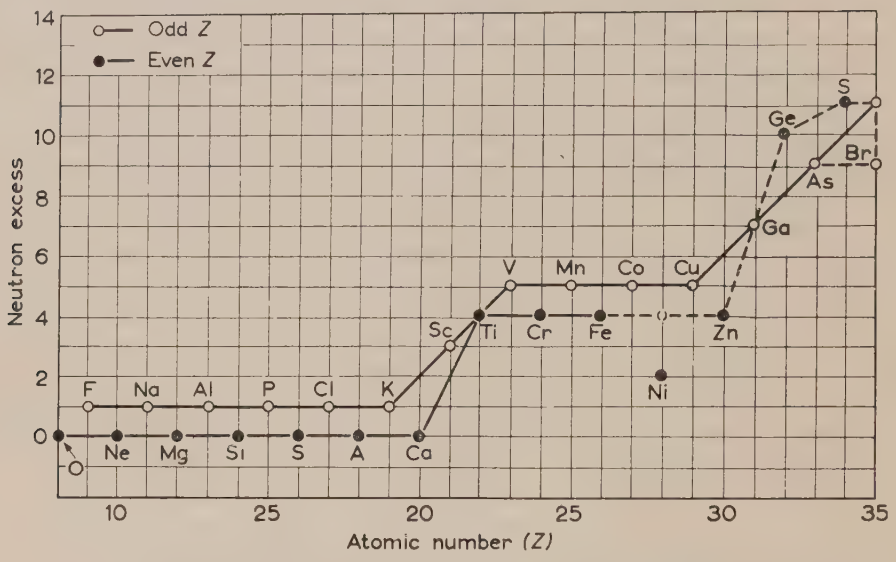

Fig. 2. Variation of neutron excess (N–Z) of the principal isotopes of odd and even Z elements with Z over the range $Z = 8$ to $Z = 35$.

Following Sc and Ti, there is again a sequence of isodiapheres (elements with uniform N–Z), similar to the $F \rightarrow K$ (odd Z) and Ne → Ca (even Z) sequences; and the next discontinuity is at Cu ($Z = 29$). The even Z curve shows a similar discontinuity at Zn ($Z = 30$), but the exceptional behaviour of the principal isotope of Ni (Fig. 2) makes this curve less satisfactory. The location of the principal isotope of Ga ($Z = 31$), which follows the Cu–Zn discontinuity, is equivalent to that of Sc, which follows the K–Ca discontinuity; and in Fig. 1 we may note that Ga, like Sc, might also be located as a valley abundance minimum. The development is, however, not so conspicuous, and there is in any case the doubt concerning the As abundance (see above); as a result, the evidence seems inconclusive with regard to a possible correlation between the N–Z discontinuity and the Ga abundance.

A third sequence of odd Z isodiapheres begins with Br* ($Z = 35$) and continues to Nb ($Z = 41$); the unstable element Tc ($Z = 43$) follows Nb. Other extended sequences of isodiapheres involving principal isotopes of odd Z elements do not appear in Fig. 3, and further attempts to correlate N–Z discontinuities

* Br^{81}, the first member of this sequence, is not the principal Br isotope; nevertheless, it is abundant (49·4%) and might in a sense not be regarded as seriously exceptional. A few other such examples may be seen in Fig. 3.

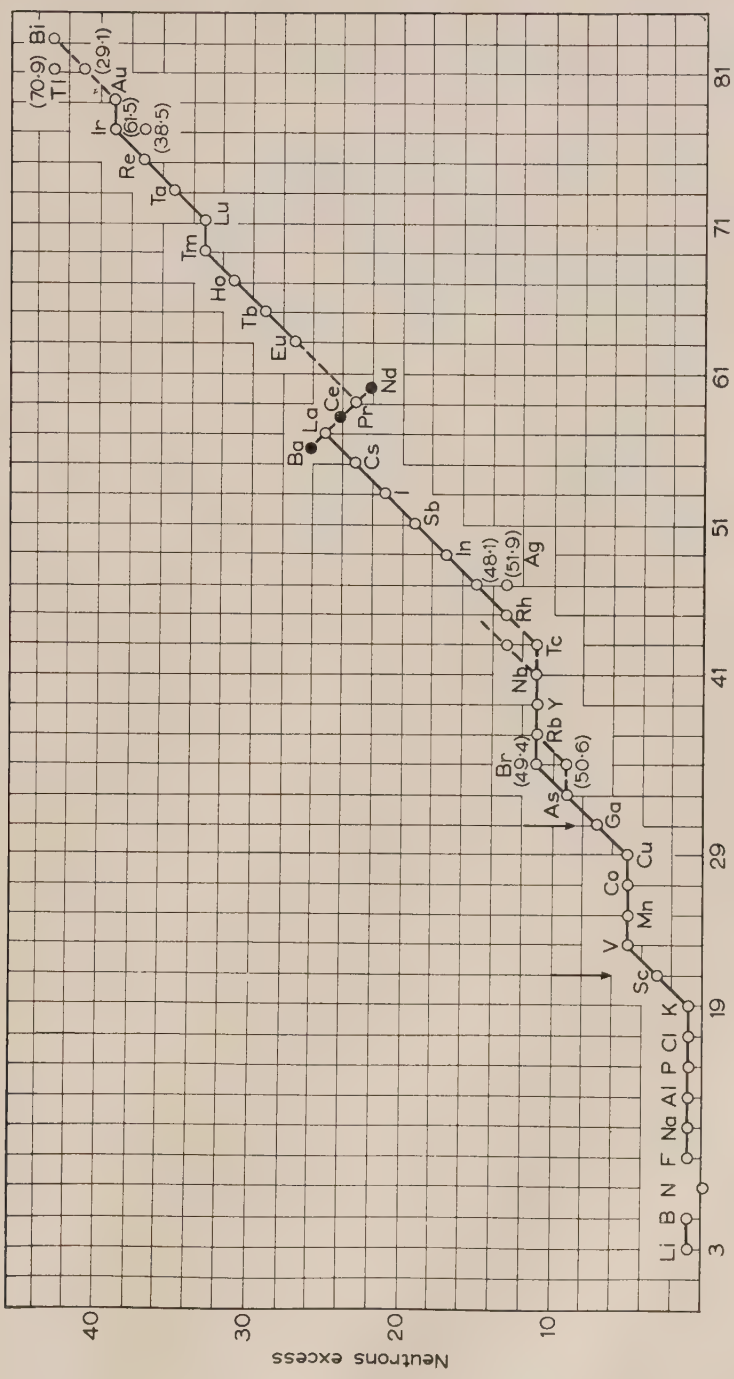

Fig. 3. Variation of neutron excess of the principal isotopes of odd Z elements up to $Z = 83$.

with abundance will not be made. We may note, however, that a second unstable element (Pm; $Z = 61$) is located after the interesting discontinuity involving the seven isotones with $N = 82$, which we consider briefly in the next discussion.

Notes on Magic Numbers and Some of the Discontinuities of Figs. 2 and 3.

Several types of evidence have been used as indicators of magic numbers; for example, an unusually large number of isotopes or isotones. (For general discussion, see Chap. 2 of Mayer and Jensen, 1955). The neutron excess is an important atomic parameter (Feather, 1952, p. 19), and if it varies fairly regularly, as in Figs. 2 and 3, discontinuities might be indicative of developments in the nucleus; accordingly, some correlation may be anticipated between magic numbers and N–Z (principal isotope).

N–Z increase following Ca^{40} is clearly correlateable with doubly magic 40 ($N = 20$, $Z = 20$); N–Z increase in the odd Z curve is similar. A similar development, that is, increase of N–Z following uniform N–Z (Ni is an exception), takes place at Zn^{64} ($Z = 30$, $N = 34$). These numbers (64, 30, and 34) are not usually regarded as primary magic numbers, but Coryell (1955), for example, has discussed the significance of 34 (either for Z or N) and 64 (total nucleons), and both these numbers appear in Zn^{64}. The discontinuity at V ($Z = 23$) on the odd Z graph involves V^{51} with $N = 28$, a favoured neutron number.

A unique development, observable only in the odd Z curve, involves the seven isotones Xe^{136}, Ba^{138}, La^{139}, Ce^{140}, Pr^{141}, Nd^{142}, and Sm^{144}, each with $N = 82$. In this well-known development, as a result of which particular significance has been attached to the neutron number 82, odd Z and even Z elements participate, and from Fig 3 it may be noted that five of the seven isotones are principal isotopes.

50 is regarded as a significant number, partly because at $Z = 50$ (Sn) a maximum of ten isotopes appear, and partly because the number (six) of isotones at $N = 50$ is unusually large, second only to the seven at $N = 82$. Moreover, three isotones, Sr^{88}, Y^{89}, and Zr^{90} at $N = 50$, are principal isotopes. These developments at $N = 50$ are similar to those noted above at $N = 82$, but not quite so marked, and no discontinuity involving $N = 50$ appears in Fig. 3.

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The chemical composition of some stony meteorites

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(*Received* 20 *September* 1955)

Abstract—New evidence is presented for the existence of two main groups among the chondrites. These are the H and L groups of Urey and Craig (1953), with 28 and 22 per cent total iron, respectively. Subdivision of the H-group into subgroups of different chemical composition is discussed. New analyses of twenty-one stony meteorites, including eleven carbonaceous chondrites, are presented.

Introduction

As early as 1878 Nordenskiöld had noted great uniformity of chemical composition of a great number of chondrites. This uniformity is especially well illustrated when the composition is expressed on an oxygen-free basis as atomic percentages in the way suggested by Wahl in 1910. In recent years the uniformity has been observed to be even more pronounced than was earlier thought. This is mainly due to better analytical methods, which give more accurate figures for the minor elements. This uniform composition, varying only in the state of oxidation, was regarded as indicating the origin of stony meteorites from different layers of the same planet, and as suggesting a similar model for our own planet.

In 1953 Urey and Craig made a compilation of all available analysis on stony meteorites. They divided them into "superior analyses," and others which on evidence gathered in recent years must be in error. Ninety-four analyses of chondrites were considered superior. Among those discarded were many old analyses and analyses in which composition differed very much from the average. From consideration of the superior analyses Urey and Craig made an interesting observation. The total iron content was found to be grouped around two distinct values, namely 28·58 per cent Fe and 22·33 per cent Fe, and these two groups could not be transferred into each other by means of oxidation or reduction. It seems then more likely that the chondrites have their origin in two planets rather than in one (Urey and Craig, *op. cit.*, p. 78). The two groups were named the high (H) and low (L) groups after their high and low iron contents. The way in which Urey and Craig made their choice of analyses has been criticized. To discard analyses, for example, because some components differ strongly from the mean, has been regarded as inconclusive. However, it must be said that no single analysis was discarded on the basis of its iron content. Common reasons for rejection of analyses were, "No alkalis, $Al_2O_3 = 0$" (Maziba), "MnO = 5·50, $Cr_2O_3 = 1·19$" (Limerick), or "No alkalis, all Fe as Fe" (Otomi), etc.

New Evidences Concerning the H- and L-groups

In spite of the above criticism, it is now evident that Urey and Craig's choice of "superior" analyses is in general correct, although the basis for discarding an analysis is in some cases unsound, and has resulted in rejection of good analyses.

Table 1. Analyses of stony

	Analyst	Fe	Ni	Co	FeS	SiO_2	TiO_2	Al_2O_3	MnO
Carbonaceous chondrites (H)									
Type I									
1. Tonk	CHRISTIE (CHRISTIE, 1914)	0·33	0·07	—	16·11[1]	22·42	0·09	1·92	0·15
2. Orgueil	Author	0·00	0·00	0·00	15·07	22·56	0·07	1·65	0·19
3. Ivuna	Author	0·00	0·00	0·00	18·38	22·71	0·07	1·62	0·23
Type II									
4. Nogoya	FRIEDHEIM (FRIEDHEIM, 1888)	0·00	0·00[3]	0·00	8·97[2]	27·18	—	2·35	0·07
5. Cold Bokkeveld	WÖHLER and HARRIS (WÖHLER, 1859 and 1860)	0·00	0·00	0·00	8·44	28·09	—	1·87	0·88
	Author	0·00	0·00	0·00	8·16	27·33	0·08	2·29	0·19
6. Mighei	Author	0·00	0·00	0·00	10·05	27·81	0·08	2·15	0·21
7. Nawapali	Author	0·00	0·00	0·00	7·67	27·08	0·09	2·09	0·17
8. Haripura	Author	0·00	0·00	0·00	14·93	26·39	0·08	2·27	0·19
9. Boriskino	ALEKSEEVA (Kvasha, 1948)	0·00	1·15	0·03	2·79[4]	26·73	0·15	3·11	0·15
10. Santa Cruz	Author	0·00	0·00	0·00	9·04	29·36	0·12	2·19	0·19
11. Murray	Author	0·00	0·00	0·00	7·67	28·69	0·09	2·19	0·21
Type III (Ornansites)									
12. Ornans	Author	0·72	—	—	6·43	33·52	—	—	0·18
13. Warrenton	Author (WAHL, 1950)	4·02	1·43	0·09	5·12	34·82	0·15	2·18	0·20
14. Lance	Author	2·19	1·50	0·07	6·49	33·23	0·13	2·93	0·20
15. Felix	Author (WAHL, 1950 partial)[7]	4·72	1·36	0·07	5·48	33·95	0·10	2·91	0·21
	FIREMAN (MERRILL, 1902)	2·59	1·15[6]	0·08	4·76	33·57	—	3·24	0·68
16. Mokoia	Author	0·00	0·00	0·00	6·74	33·40	0·10	2·51	0·19
Chondrites with 15–19 *per cent met.* Fe(H)									
17. Hainaut	Author	15·09	1·63	0·06	5·15	36·17	0·10	3·09	0·29
18. Oakley	Author (WAHL, 1950a)	15·15	1·88	0·13	6·11	36·55	0·14	1·91	0·32
19. Tromöy	Author	16·59	1·61	0·09	5·21	37·19	0·08	3·17	0·40
20. Aarhus	ME MOURITZEN	17·30	1·93	—	5·64	37·49	0·16	1·46	0·34
21. Collescipoli	Author (WAHL, 1950b)	18·30	1·56	0·10	6·23	36·21	0·18	3·67	0·31
22. Ochansk	Author	19·14	1·58	0·10	5·37	35·81	0·11	4·11	0·26
Enstatite chondrites 20–26 *per cent met.* Fe(H *and* HH)									
23. Hvittis	BORGSTRÖM (BORGSTRÖM, 1903)	20·04	1·96	0·07	7·27	41·53	—	1·55	—
24. Indarch[8]	WHITFIELD (MERRILL, 1915)	10·40	1·38	0·06	13·30	35·70	—	1·97	0·13
	Author	24·13	1·83	0·08	14·20	35·26	0·06	1·45	0·25
25. Saint-Sauveur	RAOULT (LACROIX, 1923)	25·73	1·62	0·12	14·37	33·40	—	3·29	0·06
Chondrites with 7–8 *per cent met.* Fe(L)									
26. Monte das Fortes	Author	6·88	1·18	—	6·14	39·77	0·05	3·30	0·32
27. Linum	Author	6·89	1·24	—	7·31	39·41	0·14	3·73	0·31
28. Varpaisjärvi	Author (WAHL and WIIK, 1950)	7·58	1·09	0·11	6·97	39·28	0·17	4·32	0·14
29. MCKINNEY	Author (WIIK, 1950)	7·81	0·79	0·04	6·47	39·77	0·14	3·42	0·31
30. Mern	ME MOURITZEN	8·09	1·09	—	6·24	41·38	0·17	1·26	0·17
Achondrites									
31. Norton County (Bu)	Author	0·73	0·04	—	1·37	54·40	0·06	0·61	0·16

[1] CHRISTIE reports S as sulphides 0·13 per cent, free S 1·44 per cent, and SO_3 6·90 per cent. All this S is calculated for the sake of comparison with the other analyses—to FeS.

[2] FRIEDHEIM reports 2·08 per cent SO_3 here calculated to FeS.

[3] 1·61 per cent Ni + CoO.

[4] 1·02 per cent S and 29·79 Fe_2O_3 calculated by author to FeS and FeO respectively.

[5] The material was dried at 120°C before samples were taken. In the dried material WÖHLER found 10·5 per cent water but he did not indicate it in the analysis, because he believed the water was of terrestrial origin. Author has replaced it and recalculated the analysis to 100·00 per cent.

[6] 1·01 per cent NiO was calculated to Ni.

meteorites. Weight per cent

FeO	MgO	CaO	Na_2O[9]	K_2O[9]	P_2O_5	H_2O^+	H_2O^-	Cr_2O_3	NiO	CoO	C	loss[10] of ign.	Sum	
9·40	13·71	1·34	3·24	0·36	0·11	10·74	10·92	0·12	0·86	—	2·70	—	94·59	1
11·39	15·81	1·22	0·74	0·07	0·28	19·89		0·36	1·23	0·06	3·10	6·96	100·65	2
9·45	16·10	1·89	0·75	0·07	0·41	18·68		0·33	1·34	0·06	4·83	4·10	101·02	3
20·28	19·05	2·52	0·18		0·15	10·85	3·43	0·35		2·04	1·62	—	99·04	4
23·34	20·24	1·55	1·12		Tr.	10·5		0·69	1·50	Tr.	1·52	0·23	99·97	5
20·17	18·73	1·56	0·61	0·05	0·30	15·17		0·42	1·49	0·08	1·30	2·23	100·16	5
19·13	19·46	1·66	0·63	0·05	0·30	12·86		0·36	1·53	0·07	2·48	0·36	99·19	6
20·76	17·89	2·20	0·54	0·16	0·26	16·41		0·38	1·54	0·06	2·50	2·03	101·83	7
15·12	18·04	2·01	0·70	0·07	0·23	13·70		0·45	1·71	0·08	4·00	—	99·97	8
24·54	19·35	2·22	1·07	0·20	—	8·72	2·96	0·30	—	—	—	3·75	97·22	9
22·34	21·16	2·30	0·50	0·12	0·32	9·23	1·10	0·39	1·64	0·08	2·54	—	102·62	10
21·08	19·77	1·92	0·22	0·04	0·32	9·98	2·44	0·44	1·50	0·08	2·78	0·62	100·04	11
—	23·87	1·99	0·55	0·17	0·35	0·25	0·18	0·50	0·00	0·00	—	—	—	12
24·34	23·57	2·17	0·69	0·23	0·20	0·10	0·00	0·58	0·00	0·00	0·19	—	100·08	13
24·80	23·54	2·64	0·58	0·14	0·32	1·40		0·49	0·00	0·00	0·46	—	101·11	14
22·84	23·74	2·20	0·59	0·05	0·34	0·18		0·44	0·00	0·00	0·45	—	99·63	15
26·22	19·74	5·45	0·62	0·14	—	—	0·16	0·80	0·00	—	0·36	—	99·56	15
25·43	23·98	2·56	0·51	0·04	0·38	2·07		0·52	1·64	0·08	0·47	—	100·62	16
11·14	23·30	1·89	0·76	0·15	0·00	0·87	0·00	0·30	—	—	—	—	99·99	17
10·21	23·47	2·41	0·78	0·20	0·30	0·15	0·06	0·52	—	—	—	—	100·29	18
8·26	23·64	1·79	0·72	0·11	0·31	0·59	0·03	0·45	—	—	—	—	100·24	19
7·39	24·03	1·69	1·12	0·23	0·15	0·11	0·05	0·43	—	—	—	—	99·52	20
5·94	23·42	1·18	1·31	0·24	—	0·07	0·06	0·60	—	—	—	—	99·38	21
6·90	23·10	1·59	0·66	0·15	0·23	0·24	0·02	0·15 Cr_2S_3	—	—	—	— CaS	99·52	22
0·34	23·23	0·74	1·26	0·32	P = 0·08	—	—	0·56	—	—	—	0·86	99·81	23
14·98	16·92	0·70	Tr.	0·00	0·52	2·80		—	—	—	0·31	0·60	99·77	24
0·00	17·48	0·95	1·01	0·11	0·52	1·17		0·47	0·00	0·00	0·43	0·93	100·33	24
0·21	17·00	1·12	0·96	0·21	0·17	0·09		0·15 Cr_2O_3	—	—	0·10	1·15	99·75	25
13·21	25·38	1·81	0·71	0·13	0·30	0·00	0·02	0·36	0·00	0·00	—	—	99·56	26
13·95	23·31	1·68	0·70	—	0·12	0·00	0·07	0·27	0·00	0·00	—	—	99·13	27
12·68	23·94	1·88	0·83	0·23	0·28	0·21	0·10	0·66	0·00	0·00	—	—	100·47	28
12·82	23·82	1·79	0·75	0·22	0·27	0·44	0·14	0·51	0·00	0·00	—	—	99·51	29
11·57	25·83	2·00	1·20	0·18	0·05	0·24	0·00	0·14	0·00	0·00	—	—	99·61	30
0·00	40·72	0·66	0·13	0·04	0·02	0·19	0·17	0·07	0·00	0·00	—	CaS 0·37	99·74	31

[7] A partial analysis of Felix was made by the author and published by WAHL in 1950. It differs in some details from the one now presented. The material was from a different source.

[8] Indarch has formerly been listed as a carbonaceous chondrite. From the new analysis it is evident that Indarch is an enstatite chondrite closely related to Saint-Sauveur.

[9] Some of the values for alkalies have been determined by GEORGE EDWARDS and JEANNE INGERSOLL, using the method of EDWARDS and UREY (1955). These are the values for the following stones: Orgueil, Ivuna, Cold Bokkeveld, Mighei, Haripura, Murray, Felix, Mokoia, and Indarch. The other carbonaceous chondrites and Tromöy were made with flame photometer by the author. All other of author's alkalies—and ME MOURITZEN'S—have been determined using the J. L. SMITH method.

[10] Loss of ignition reduced with H_2O, C, and S. The oxidation of Fe, FeO, Ni, and Co taken into consideration. This number is an approximate estimation of the amount of organic matter.

One example is the analysis of Orgueil by Pisani. It was discarded because 13·43 per cent FeS was reported. This very high number for FeS is now shown to be correct, and even somewhat too low (Table 1). It may be worth noting here that high sulphur contents are by no means rare among the carbonaceous chondrite group to which Orgueil belongs, as is shown below.

The H- and L-groups seem in every case to be real and well grounded. In Table 1 is shown all complete meteorite analyses previously carried out by the author. In Table 2 the results are shown on a water-, sulphur-, and carbon-free basis. In Fig. 1 the iron contents are plotted in essentially the same way as that employed by Urey and Craig, except that atomic percentages are used here, while Urey and Craig plotted their values in weight per cent. One other variation has been introduced. The present data are plotted on a water-, sulphur-, and carbon-free basis. On this basis the carbonaceous chondrites are directly comparable with the analyses of all the other groups of stones. This would not be so if the volatile constituents were included in the analyses. Only two analyses do not fall into the H- or L-groups, and no single one lies between them, as will be seen from Fig. 1. The two analyses which lie distinctly outside the high or low groups are Norton County and Indarch. Norton County is an achondrite consisting almost entirely of enstatite. The achondrites are extremely variable in chemical composition in accordance with their variation in mineralogical composition. Indarch has more iron than the meteorites of the H-group. It has been listed as a carbonaceous chondrite (Merrill, 1915), but it is evident from the present analysis that it should be listed among the enstatite chondrites. That Indarch is closely chemically related to the enstatite chondrites was pointed out once formerly (Wahl and Wiik, 1951). The analysis of Saint-Sauveur by Raoult (Lacroix, 1923) is analogous. These two enstatite chondrites alone form a group different in chemical composition from the other enstatite chondrites. They might be termed the HH-group, because of their high iron content—the highest among the stony meteorites.

Two Danish meteorites analysed by Me Mouritzen have been plotted in Fig. 1. They are included because the method of analysis is exactly the same as that employed in the present analysis. The author is grateful to Miss Me Mouritzen for permission to use these results. The advantage of comparing analyses made by the same analyst using the same method is that, if errors of absolute value occur, they probably apply to individual analyses in equal measure and direction. In Fig. 1 are plotted three carbonaceous chondrites not analysed by the author (Tonk, Nogoya, and Boriskino). The carbonaceous chondrites are of special interest for this interpretation, and for this reason all complete analyses on carbonaceous chondrites were plotted. Some of the analyses carried out by the author have been made for private persons and institutions over a period since 1948. They have been made for purposes other than those of interest in this paper, and have not been selected in any way.

Fig. 1 clearly shows that there are two well-defined main groups of stony meteorites which cannot be transferred into each other by changes in the state of oxidation. The 28·58 per cent total iron in the high group, as in Urey and Craig, is somewhat too high. 26 per cent is a more correct figure. From Tables 1 and 2 uniformity of chemical composition within these groups can be seen. Small

Table 2. Atomic percentages on water, carbon, and sulphur-free basis

	Fe total	Fe met.	Fe in FeS	Fe as oxid.	Ni	Co	Si	Ti	Al	Mn	Mg	Ca	Na	K	P	Cr	Sum
Carbonaceous chondrites																	
Type I																	
1. Tonk	26·09	0·48	14·94	10·67	1·04	—	30·44	0·11	3·07	0·17	27·72	1·95	8·53	0·62	0·13	0·13	100·00
2. Orgueil	27·34	0	14·20	13·14	1·37	0·07	31·12	0·09	2·68	0·22	32·48	1·81	1·97	0·12	0·33	0·40	100·00
3. Ivuna	27·41	0	16·82	10·59	1·44	0·07	30·43	0·09	2·56	0·26	32·14	2·71	1·95	0·11	0·47	0·36	100·00
Type II																	
4. Nogoya	26·68	0	7·10	19·58	1·89	—	31·40	—	3·20	0·07	32·78	3·11	0·40	0·00	0·15	0·32	100·00
5. Cold Bokkeveld[1]	26·28	0	6·53	19·75	1·41	0·08	32·02	0·09	3·17	0·19	32·67	1·96	1·37	0·07	0·30	0·39	100·00
6. Mighei	26·18	0	7·87	18·31	1·41	0·06	31·85	0·09	2·90	0·19	33·19	2·04	1·40	0·07	0·29	0·33	100·00
7. Nawapali	26·76	0	6·20	20·56	1·47	0·06	32·07	0·10	2·92	0·17	31·56	2·79	1·24	0·24	0·26	0·36	100·00
8. Haripura	27·00	0	12·05	14·95	1·63	0·08	31·19	0·09	3·16	0·19	31·76	2·54	1·60	0·10	0·23	0·43	100·00
9. Boriskino	25·46	0	2·16	23·30	1·34	0·03	30·36	0·16	4·16	0·14	32·73	2·70	2·36	0·29	—	0·27	100·00
10. Santa Cruz	26·56	0	6·60	19·96	1·41	0·07	31·39	0·12	2·12	0·17	33·69	2·63	1·04	0·17	0·30	0·33	100·00
11. Murray	26·13	0	5·97	20·16	1·38	0·08	32·70	0·10	2·26	0·19	33·56	2·34	0·49	0·05	0·32	0·40	100·00
Type III (Ornansites)																	
13. Warrenton	25·72	4·07	3·29	18·36	1·38	0·08	32·77	0·14	2·42	0·16	33·03	2·19	1·25	0·27	0·16	0·43	100·00
14. Lancé	25·97	2·22	4·18	19·57	1·45	0·07	31·36	0·11	3·25	0·16	33·10	2·67	1·07	0·17	0·26	0·36	100·00
15. Felix[1]	26·17	4·76	3·51	17·90	1·31	0·07	31·85	0·09	3·22	0·17	33·18	2·21	1·07	0·06	0·27	0·33	100·00
16. Mokoia	24·82	0	4·41	20·41	1·29	0·06	32·08	0·09	2·84	0·16	34·32	2·64	0·95	0·05	0·31	0·39	100·00
Chondrites with 15–19 per cent met. Fe																	
17. Hainaut	26·53	14·82	3·21	8·50	1·52	0·05	33·01	0·07	3·32	0·22	31·68	1·85	1·35	0·18	—	0·22	100·00
18. Oakley	26·32	14·79	3·79	7·74	1·74	0·12	33·17	0·10	2·04	0·25	31·72	2·34	1·37	0·23	0·23	0·37	100·00
19. Tromöy	25·58	16·12	3·22	6·24	1·49	0·08	33·61	0·05	3·38	0·30	31·82	1·73	1·26	0·13	0·24	0·33	100·00
20. Aarhus	25·75	16·71	3·46	5·58	1·79	—	33·91	0·14	1·55	0·26	32·34	1·63	1·96	0·25	0·12	0·30	100·00
21. Collescipoli	26·03	17·73	3·84	4·46	1·44	0·09	32·62	0·12	3·90	0·24	31·43	1·14	2·28	0·28	—	0·43	100·00
22. Ochansk	27·16	18·62	3·32	5·22	1·46	0·09	32·38	0·07	4·38	0·20	31·11	1·54	1·16	0·17	0·17	0·11	100·00
Enstatite chondrites																	
23. Hvittis	24·16	19·43	4·48	0·25	1·81	0·06	37·43	—	1·64	—	31·18	0·71	2·20	0·37	0·14	0·30	100·00
24. Indarch[1]	34·04	24·78	9·26	0·00	1·79	0·08	33·68	0·05	1·63	0·20	24·87	0·96	1·87	0·14	0·42	0·27	100·00
25. Saint Sauveur	36·53	26·84	9·51	0·17	1·61	0·12	32·40	—	1·28	0·05	24·56	1·17	1·81	0·26	0·14	0·08	100·00
Chondrites with 7–8 per cent met. Fe																	
26. Monte das Fortes	20·62	6·75	3·80	10·07	1·10	—	36·28	0·03	3·55	0·25	34·50	1·77	1·26	0·15	0·23	0·26	100·00
27. Linum	22·23	6·85	4·61	10·77	1·17	—	36·41	0·12	4·06	0·24	32·08	1·66	1·23	0·50	0·10	0·20	100·00
28. Varpaisjärvi	21·44	7·44	4·34	9·66	1·01	0·10	35·80	0·15	4·64	0·11	32·50	1·83	1·47	0·26	0·22	0·47	100·00
29. McKinney	21·79	7·75	4·15	9·89	0·75	0·04	36·67	0·12	3·72	0·24	32·72	1·77	1·34	0·25	0·21	0·38	100·00
30. Mern	20·53	7·89	3·86	8·78	1·01	—	37·53	0·15	1·35	0·13	34·90	1·94	2·11	0·21	0·04	0·10	100·00
Achondrite																	
31. Norton County (Bu)	0·44	0·16	0·28	0·00	0·03	0·00	46·36	0·04	0·61	0·11	51·69	0·41	0·21	0·04	0·01	0·05	100·00

[1] Of the duplicate analyses listed in Table 1 only those made by the author are listed here.

variations may very well be partly accounted for by errors in sampling and analysis. Imperfect sampling is the cause of many of the unexplained deviations from the mean. It is clear that an analysis of, for example, a 10-gram fragment of a coarse and often brecciated stone, cannot be representative of the whole, and the rarity of the material frequently makes such analysis necessary. For many meteorites

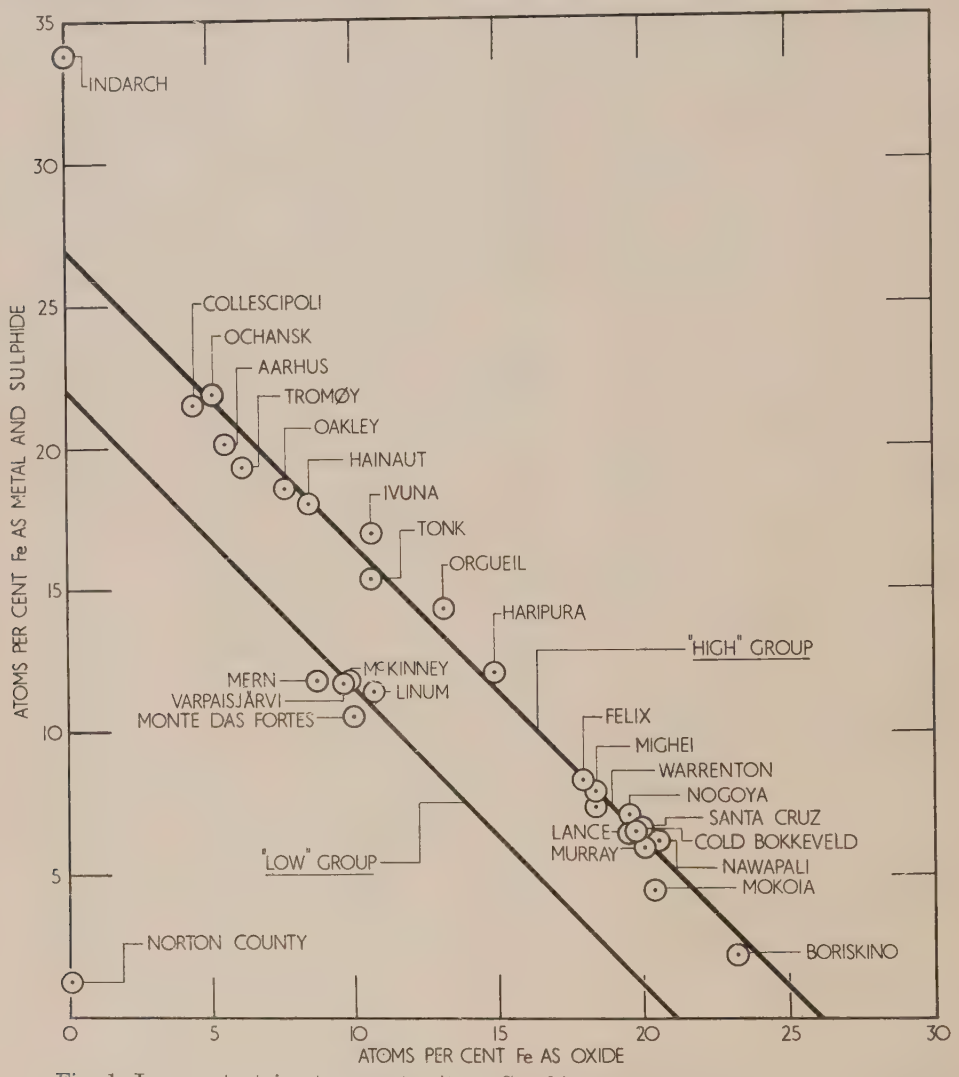

Fig. 1. Iron content in stony meteorites. Graphic representation of data in Table 2. The figures are atomic percentages on volatile free basis.

the sample should be even larger than for analysis of igneous and metamorphic rocks, as the minerals are extremely unevenly distributed. The achondrite, Norton County, is a suitable example. Due to to the generosity of Professor Lincoln LaPaz, one half-kilogram of the stone was made available for chemical analysis. In the course of crushing and grinding the whole sample, only three small rounded

fragments of metallic nickel-iron were found. The metal amounted to 0·73 per cent by weight, of the whole. In an analysis of a 10-gram sample, this metallic Fe would very probably never have been detected. Analytical errors, even in much less complicated silicate analyses than those of meteorites, are still surprisingly great, as is shown by the investigation of FAIRBAIRN and co-workers (1953).

THE COMPOSITION OF THE CARBONACEOUS CHONDRITES, SUBDIVISIONS OF THE "HIGH" GROUP

The fact that the carbonaceous chondrites all belong to the high group is of special interest. They are therefore considered at some length here.

The carbonaceous chondrites have more free carbon and usually more water and sulphur than the ordinary chondrites. The nature and amount of carbon compounds is of great interest. The state of oxidation is high. The stones very easily disintegrate into a loose powder. This occurs so easily that it is almost impossible to make thin sections for mineralogical investigation. BERZELIUS, who made the first complete general analysis of a carbonaceous chondrite in 1834 (Alais, fallen in 1806) thought at first that the specimen was not meteoritic. The 17 per cent water reported earlier by THENARD was doubted by BERZELIUS. However, water in amounts of this magnitude is not at all unusual in carbonaceous chondrites. In all reported analyses, including those recently conducted by the author and recorded in this paper, the water is distilled out in the presence of an oxidizing agent. The water reported is therefore the total oxidized hydrogen, involving the water bound as $(OH)^-$ in minerals and the water formed by combustion of organic compounds. It is remarkable that hydrated minerals occur in the carbonaceous chondrites. The first hydrated mineral (chlorite) found in a meteorite was in the carbonaceous chondrite Staroje Boriskino (KVASHA, 1948).

Knowledge of the chemical and mineralogical composition of this group of meteorites is still imperfect. In fact, of the twenty known carbonaceous chondrites, seventeen have been chemically investigated. Complete analyses are reported for only six. These are Cold Bokkeveld, Felix, Indarch, Nogoya, Staroje Boriskino, and Tonk. All of these are reproduced along with the present results in Table 1. There are in addition incomplete analyses of the seven stones, Alais, Kaba, Lancé, Orgueil, Mighei, Mokoia, and Murray.

BOATO (1954), in the course of isotopic analysis of carbon and hydrogen in twelve carbonaceous chondrites, determined total carbon and hydrogen (reference is made to his results below). Among these stones were Haripura, Ivuna, Nawapali, and Santa Cruz, not previously subjected to any chemical measurements. The true nature of some of these stones listed as carbonaceous chondrites is doubtful. Grazac, originally described as a carbonaceous chondrite by DAUBRÉE and ST. MEUNIER, has been re-investigated by LACROIX, who doubts its meteoritic origin. The meteoritic origin of Simonod is similarly doubted. Crescent has not been investigated at all, but it is listed as carbonaceous (PRIOR-HEY'S catalogue, 1953).

A careful investigation of the organic compounds in Cold Bokkeveld has been published by G. MUELLER (1952). All other discourses concerning the organic compounds in carbonaceous chondrites consist of vague remarks such as: "A

spice-smelling compound was obtained" or "a white sublimate without smell was obtained" or "a greasy substance was left after extraction with ether and treatment on steambath." In fact, the organic compounds are the least-well-known substances in the carbonaceous chondrites. This is partly due to the fact that only very small amounts of these rare materials are obtainable by extraction.

The author conducted some new analyses of the carbonaceous chondrites. Attention was directed mainly towards the major elements. These new analyses are listed in Tables 1 and 2. The material was that left over from Boato's work (*op. cit.*), and the original sources of the meteorites are listed in his publication.

It is evident that there are three types of carbonaceous chondrites, and they have been grouped in this way in Table 1.

The first type, of which Orgueil, Ivuna, and Tonk are examples, have nearly 20 per cent water (all H as H_2O), 22 per cent SiO_2, and 15–18 per cent FeS. All S is calculated as FeS, although it is evident that small amounts of S are bound in organic compounds. In fact, some sulphur occurs as SO_3. They have no metallic nickel-iron. It is very probable that Alais also belongs to this sub-group. The results of analysis by Thenard and Berzelius are indicative of this, though it is difficult to express theirs in the modern form. It is unfortunate that only a few grams of the first observed fall of a carbonaceous chondrite is preserved.

Cold Bokkeveld is representative of the second sub-group. The group includes Cold Bokkeveld, Nogoya, Mighei, Nawapali, Haripura, Santa Cruz, Murray, and Boriskino. Sub-group II is characterized by about 13 per cent water, 27·5 per cent SiO_2, and 9 per cent FeS. Again there is no metallic nickel-iron.

The third group is well represented by Felix. Sub-group III includes Lancé and Mokoia. Ornans and Warrenton have the same chemical composition and the same appearance as these three stones of the third group, and all five could be termed Felix-type carbonaceous chondrites, or ornansites. The third group have 33–34 per cent SiO_2, less than 1 per cent water, and the "normal" amount of FeS in chondrites, namely 5–6 per cent. They have small amounts of metallic nickel-iron.

The second group is chemically almost the arithmetic mean between the first and the third, as shown in Table 3.

Calculated on a volatile-free basis, all carbonaceous chondrites have practically the same composition, and belong to the H group in their total Fe content. This is clear from Table 2.

Table 3. Mean values of certain constituents in sub-groups of carbonaceous chondrites

Sub-group No.	Names	SiO_2	MgO	FeO	C	H_2O	FeS
I	Orgueil, Tonk, Ivuna	22·56	15·21	9·77	3·54	20·08	16·52
II	Cold Bokkeveld, Nogoya Mighei, Nawapali, Haripura, Boriskino, Santa Cruz, Murray	27·57	19·18	20·28	2·46	13·35	8·66
III	Felix, Lancé, Mokoia, Warrenton, Ornans	33·58	23·74	24·20	0·46	0·99	6·05
	$\frac{\text{Type I} + \text{Type III}}{2} =$	28·07	19·47	16·99	2·00	10·54	11·28

Boato (*op. cit.*) reports in many cases less water in the carbonaceous chondrites than that found in the present investigation. Boato used a combustion-distillation method. Pennfield tubes were used in the present work with carefully dried PbO_2 as oxidant and trap for the sulphur. The material for analyses was the same as Boato's. The Pennfield method tends to give somewhat low values, and never too high ones, and the reason for the disagreement of the results is not clear.

The relationship between all the meteorites of the high group seems to be as follows:

1. The carbonaceous chondrites of the Orgueil type (I)

$\xrightarrow{-H_2O,\ S\ and\ org.\ matter}$

2. The carbonaceous chondrites of the Cold Bokkeveld type (II)

$\xrightarrow{-H_2O,\ S,\ O,\ and\ org.\ matter}$

3. The carbonaceous chondrites of the Felix type (or the ornansites) (III)

$\xrightarrow{-O}$

4. The chondrites with 15–19 per cent metallic Fe

$\xrightarrow{-O}$

5. The enstatite chondrites of the Hvittis type

This is intended only to give a picture of the chemical relations between the subgroups, and not intended to suggest the genesis. There is insufficient evidence at the moment to permit any clear conclusions regarding the genesis of various groups of meteorites.

The discontinuity in this series is interesting. The degree of oxidation, the

Table 4. Metallic Fe, weight per cent in the H and L groups.
All determinations with the $HgCl_2 \cdot NH_4Cl$ extracting method.

	Per cent met. Fe		Per cent met. Fe
The H group		*The H group—contd.*	
Orgueil	0	Hainaut	15·09
Ivuna	0	Oakley	15·15
Cold Bokkeveld	0	Tromy	16·59
Mighei	0	Aarhus	17·30
Nawapali	0	Richardton	17·41
Haripura	0	Forest City	18·29
Santa Cruz	0	Collescipoli	18·30
Murray	0	Ochansk	19·14
Ornans	0·72	*The L group*	
		Monte das Fortes	6·88
Oubari	1·80	Linum	6·89
Lancé	2·19	Holbrook	7·05
		Varpaisjärvi	7·58
Warrenton	4·02	McKinney	7·81
Guidder	4·37	Mern	8·09
Waconda	4·71		
Felix	4·72		

water and sulphur contents, form well-defined steps, and all the other components behave similarly. To date, no examples of any diffuse transitions from one subgroup to another have been found. Accordingly, the mineralogical composition must also be of this discontinuous form. The only quantitative mineralogical factor examined here is the metallic iron-nickel content. This shows clearly the discontinuity in the degree of oxidation (Table 4). Only the metallic Fe is recorded in this table. The content of nickel is almost constant.

In Table 4 are to be found some stones not listed in Tables 1 and 2. Only partial analyses were made in these cases. It will be seen from the Table that there are discontinuities in the states of oxidation. A surprising feature is that the values seem to form an approximately geometric series. The grouping of the results around numbers 2, 4, and 16 per cent may be quite accidental. Certainly the number of results is insufficient to merit any far-reaching conclusion.

The low group seems to have only one oxidation state. The FeS content is also very constant, and accordingly all the points representing this group are gathered in a small area in Fig. 1. It is surprising that only the high group exhibits variation in the state of oxidation, while the low group has a constant oxidation state. Further investigation may show greater variation in the low group than is exhibited by the present results.

Appendix

The way to present chemical analyses of stony meteorites. Some remarks on Table 1

The composition of stony meteorites, as presented in Table 1, shows the cations as oxides, sulphides, etc. This system is conventional, and does not in all cases give a true representation of the composition, because the chemical analysis does not furnish the necessary mineralogical facts. For example, all S is calculated to FeS, in spite of the fact that in many meteorites there are small amounts of (Ca, Mn)S (oldhamite) and $FeCr_2S_4$ (daubreélite), and, in carbonaceous chondrites, even small amounts of "organic" sulphur. The amounts of these minerals would have to be known in order to place properly S as well as Cr and Ca. The mineralogical, quantitative analysis is difficult to obtain. Oldhamite can be extracted with water, but the operation is hardly quantitative because of the Mn content. CaO can be found in almost all water extracts from stony meteorites, particularly from the enstatite chondrites. The author believes therefore that oldhamite is a far more common constituent in stony meteorites than was formerly supposed. Phosphorus is another element that is equally difficult to place. If it occurs mainly as schreibersite, $(Fe, Ni, Co)_3P$, it should be listed as P, but if it occurs as merrilite and/or apatite it should be listed as P_2O_5. The author believes that schreibersite scarcely occurs in stony meteorites. There are two reasons for this. (1) P forms minerals with Ca, Al, and Na much more easily than it does with Fe, Ni, and Co, and therefore is exhausted before there is an opportunity for schreibersite to form. Actually, schreibersite has been reported by chemists dealing with Fe meteorites; however, in these there is, of course, no Al, Ca, or Na. (2) The author's experience is that the amount of nickel extracted from the sample with $HgCl_2 \cdot NH_4Cl$ (the metallic Ni) is, within the limits of accuracy, always the same as the total Ni obtained from the main analysis. Should schreibersite occur, the total Ni would have to be greater. NiO can occur only when no metallic Fe is present. This happens, for example, in the carbonaceous chondrites in which there are no metallic Fe, Ni, Co to extract, and accordingly we cannot make any comparison between the metallic and the total nickel. In this case there is therefore no evidence to show whether schreibersite occurs or not.

Another difficulty with Table 1 is the uncertainty in the oxidized state of Fe. The amount of FeO is only a calculated number obtained by subtraction of the metallic iron and the troilite iron from the total iron. The FeS tends to be too high, because all S was calculated to that compound. Accordingly, the FeO tends to be too low. It is almost impossible to determine FeO

directly, because of the presence of readily soluble sulphides, metallic iron, and organic compounds. When we try to dissolve the sample for FeO titration, all iron is reduced to FeO, and the total iron rather than the true FeO is obtained. (The small amounts of iron in chromite and carbides are not dissolved in acids, therefore the total iron determined in this manner is somewhat too low. The correct total iron is obtained from the main analysis.) Fe_2O_3 should be obtained by subtraction of FeO, Fe metal, and Fe in FeS from the total iron, but because the FeO is not known, the Fe_2O_3 cannot be determined either. In fresh meteorites containing metallic iron, ferric iron is supposed not to occur. This is probably true. It is difficult to understand that iron should be found in three different oxidation states in the same stone. Where metallic iron does not occur, however, it is very possible that there is some Fe_2O_3. Actually there seems to be some magnetite in the carbonaceous chondrites as indicated by the X-Ray powder pattern (Dr. Urey, private communication). The chlorites reported in carbonaceous chondrites (Kvasha, *op. cit.*) can hardly be without ferric iron either. It is most unfortunate that ferric iron cannot be determined.

There have been attempts to create rules for calculating the mineralogical composition of stony meteorites from the chemical analyses. These have not been intended to represent the actual mineral composition, but a kind of "norm" for stony meteorites. Such a norm is inherently too misleading to be useful, because of the imperfections in the presentation of the analysis and the complicated mineralogy of meteorites. It is impossible to make a normative calculation to represent the true mode without knowing the Fe/Mg ratio in the co-existing pyroxenes and olivines (the ratio is not the same in both minerals, as was formerly supposed), and without knowing the location of the Ca and Al, which are not found exclusively in feldspars. This norm must therefore be even more misleading than that calculated from igneous and metamorphic rocks by the C.I.P.W. system.

Acknowledgements—I wish to extend my gratitude to Dr. Harold C. Urey, who suggested a closer investigation of the carbonaceous chondrites. I am also indebted to many institutions and private persons for analytical material, and for permission to use as yet unpublished data. With Dr. George Edwards and Mr. O. Joensuu of the University of Chicago, I had fruitful discussions. I am indebted to Mr. E. P. Henderson from United States National Museum, and to Dr. C. R. Naeser from U.S. Geological Survey, for critically reading the manuscript. This research was supported by the National Science Foundation.

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GEOCHEMICAL NOTES

An interpretation of the Rhodesia and Witwatersrand age patterns

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(*Received 5 November* 1955)

IN two recent papers, AHRENS (1955a, 1955b) reported some interesting regularities in the discordant uranium-lead ages of uraninite and thucholite from the Witwatersrand, and in some very ancient monazite and uraninite samples from the Canadian and Rhodesian shields. He found that, when he plotted the isotopic analyses of these samples on D/P

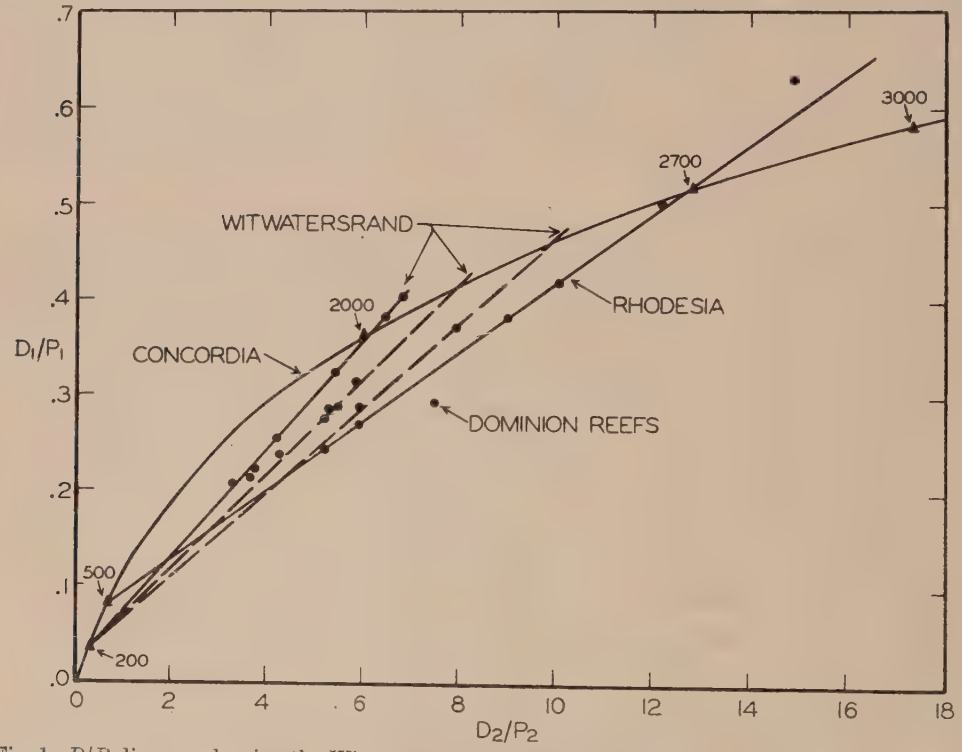

Fig. 1. D/P diagram showing the Witwatersrand and Rhodesia regularities found by AHRENS. D_1 and D_2 are the mole concentrations of the daughter isotopes, Pb^{206} and Pb^{207} respectively, while P_1 and P_2 refer to the mole concentrations of the parent isotopes, U^{238} and U^{235}. The curve marked "concordia" is the locus of all points such that $t_{U\text{-}235} = t_{U\text{-}238}$.

diagrams (Fig. 1), most of the points lay on straight lines. AHRENS felt that "a well-ordered age array suggests that physical causes, rather than chemical, have controlled lead loss," and refers to a private communication by MAYNE that "this opens up a possibility that some other, not properly understood, nuclear process could conceivably be the cause." In this note it is shown that there is at least one simple geochemical process which will

produce these age patterns. In Fig. 1 the experimental points are those discussed by AHRENS. The solid straight lines through these points are theoretical curves calculated by assuming that the true age of the Rhodesia samples is 2700 million years and varying amounts of lead were lost (or uranium was gained) 500 million years ago, and by assuming that the Witwatersrand samples are 2040 million years old (AHRENS, 1955b) and have lost lead or uranium 200 million years ago. The dashed straight lines are similar curves calculated for ages 2250 and 2450 million years. In the case of the monazite samples, one might expect that the assumption of a given Pb^{206} and Pb^{207} loss would imply a proportionate loss of Pb^{208}, and therefore, that the same correction for lead loss would bring all three ages into agreement. However, TILTON (1955) has shown that the thorium-lead is not homogeneously mixed with uranium-lead in monazite crystals, and large fractionations occur during leaching. Therefore, there should not be this simple relationship between the thorium-lead and the uranium-lead ages.

The excellent fit of the Witwatersrand main regularity to the theoretical curve is good evidence that these widely separated samples underwent a similar geological history, and is in agreement with the interpretation that they were formed 2040 ± 50 million years ago and suffered loss of lead because of some alteration or leaching process 200 ± 150 million years ago. The minor regularities are fitted less well by the dashed curves. If the minor regularities are real, they could therefore be interpreted as two groups of minerals having true ages of 2250 and 2450 million years and which have also lost varying amounts of Pb 200 million years ago. A similar statement can be made for the Rhodesia and Madagascar samples. It is rather doubtful that the Huron Claim samples can actually be identified with those from Rhodesia on the basis of this evidence, especially in view of the fact that only one of them falls on the theoretical curve, and this might well be coincidental.

Thus it seems that the regularities found by AHRENS can be more simply explained by chemical leaching or alteration at a single episode in geological history rather than "control of lead loss by physical processes which perhaps have operated at varying degrees but a uniform rate ever since the minerals were formed," as suggested by AHRENS.

The more difficult question of the uniqueness of the interpretation requires the results of a more general theoretical discussion, which is presently being prepared. It may merely be stated that aside from the possibility of the regularities being coincidental, there are a very limited number of similar geochemical processes which will produce regularities of this sort. All of these involve episodic uranium-lead fractionations at the times mentioned. Plausible arguments can be given for expecting that the interpretation given here is the correct one, although the available data are not sufficient to settle the question finally. In the case of the Rhodesia samples, there is good independent evidence from Rb-Sr and K-A determinations on Bikita lepidolite (WETHERILL, ALDRICH, and DAVIS, 1955) that the interpretation is correct in this case.

The properties of the other type of diagram used by AHRENS, the semilog plot, are similar to those of the D/P diagram, but this diagram is less useful for recent times, when lines that are straight on the D/P diagram become highly curved. For example, less of constant lead-lead age are straight lines passing through the origin on the D/P diagram, while these lines go to –00 on the semilog plot.

If this recent lead loss is accepted as the physical basis of the convergent age patterns of AHRENS, it is clear that the convergent age of a single sample has little meaning. Consider the Dominion Reefs uraninite for which AHRENS tentatively determines a convergent age of 2930 million years. If this sample had a true age of 2930 million years and lost lead 500 million years ago, it would have the lead-uranium ratios found. However, if the true age were 2730 million years and a single episode of lead loss took place in modern times, the same lead-uranium ratios would be found. Actually there are infinite number of possibilities.

It is only when a large number of samples are available, as in the case of the Witwatersrand main regularity, that a plausible argument can be made concerning the true age of the samples and their probable geological history.

The discovery of these regularities and their possible explanation raises the rather exciting possibility that it may be possible to use discordant uranium-lead ages to determine some aspects of the common geologic history of large areas, even entire geological provinces.

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New determinations of the age of the Bob Ingersoll pegmatite, Keystone, S. Dakota

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(*Received* 8 *December* 1955)

Abstract—Age determinations have been made on various minerals from the Bob Ingersoll pit No. 1. The uranium-lead ages agree at 1600 m.y.; Rb-Sr ages of microcline, muscovite, and lepidolite are all about 2050 m.y., probably indicating that the currently accepted Rb decay-constant is incorrect. K-A ages of the micas are in fairly good agreement with U-Pb ages when a K^{40} branching ratio of 0·100 is used. The K-A age of the microcline is definitely lower, probably indicating loss of argon from this mineral.

Introduction

The literature records different ages for the Bob Ingersoll pegmatite in the Black Hills region of South Dakota. Davis and Aldrich (1953) have reported 2000 m.y. for the age of a lepidolite from this pegmatite. Other lepidolite ages which have been reported are 1390 m.y. (Tomlinson and Das Gupta, 1953) and 850 to 1500 m.y. (Ahrens, 1949). No uranium-lead ages with isotopic analysis of lead have been reported. C. W. Davis (1926) published a bulk chemical analysis of uraninite from the Ingersoll pegmatite and calculated a uranium-lead age of 1667 m.y. However, his data give an age of 1400 m.y. when recalculated, using modern decay-constants for uranium and thorium. A description of the geology of the area has been given by Page and others (1953).

In this paper a number of new age measurements on minerals from this pegmatite are presented in order to help elucidate the nature and origin of these discrepancies, and to demonstrate the relative validity of different methods of age determination.

Uranium-lead and Thorium-lead Age Determinations

The element uranium has two radioactive isotopes U^{235} and U^{238}, with different half-lives, and it is possible to use both of these decay systems for mineral age determinations. If a mineral does not undergo chemical alteration during geologic time, the ages calculated from these two decay systems will be concordant, i.e. will be in agreement. On the other hand, if a mineral undergoes losses or gains of uranium or lead during geologic time, the U^{238}-Pb^{206} age will not, in general, agree with the U^{235}-Pb^{207} age, nor will either of these

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"ages" be the true age of the mineral. Occasionally, concordant ages might result from an accidental combination of these geochemical processes, but this accidental agreement should be rare. Some minerals (e.g. zircon, monazite, microlite) give discordant ages so frequently that an occasional concordant age for these minerals raises the question that this may possibly be such a case of accidental agreement. However, WASSERBURG and HAYDEN

Table 1. Ages of uraninite from the Bob Ingersoll pit No. 1 Keystone, S. Dakota

U^{238}-Pb^{206}	U^{235}-Pb^{207}	Pb^{207}-Pb^{206}	Th^{232}-Pb^{208}
1580 ± 30 m.y.	1600 ± 20	1630 ± 30	1440 ± 75

Table 2. Analysis of uraninite

Element	Conc'n (weight per cent)
Uranium	64·55 ± 0·64
Thorium	2·93 ± 0·04
Lead	17·01 ± 0·5

Table 3. Isotopic data for lead

Isotope	Conc'n in uraninite (per cent)	Mole ratio to 206 × 100
Pb^{204}	0·00045 ± 0·00007	0·0030 ± 0·0005
Pb^{206}	15·28 ± 0·30	100
Pb^{207}	1·517 ± 0·037	9·90 ± 0·10
Pb^{208}	0·213 ± 0·005	1·38 ± 0·014

(1955) have shown that their fresh samples of uraninite consistently gave concordant U^{238}-Pb^{206} and U^{235}-Pb^{207} ages. Similar results have been found in this laboratory, in four out of five cases. Therefore, it seems that these alteration processes are less common for this mineral. Thus, when the U^{238}-Pb^{206} and U^{235}-Pb^{207} ages agree for a fresh sample of uraninite, this age is probably the true age of the mineral.

A crystal of uraninite weighing approximately 250 g was collected in the summer of 1954. The crystal was broken open and a fragment weighing 70 mg and which was free of any microscopically visible alteration was selected for the analyses reported in this paper. Uranium was determined both by isotope dilution, using U^{235} as a tracer, and by a colorimetric procedure, using dibenzoylmethane, which was almost identical to that developed by ADAMS and MAECK (1954). The colorimetric procedure used for thorium followed closely the techniques already described by TILTON, ALDRICH, and INGHRAM (1954). Lead was determined by isotope dilution, using a tracer enriched in Pb^{208} and isolating lead by dithizone extractions. Mass spectrometer runs were made with 10–20 μg of lead, using surface ionization.

The results of the determinations are given in Tables 1 to 3. The accuracies stated are

conservative estimates of the probable errors, including all errors other than those which may arise from incorrect decay-constants or from unknown effects of the pegmatite's geological history. The uranium content of the uraninite was taken to be the average of the mass spectrometric and colorimetric determinations, which were 64·12 and 64·97 per cent respectively. Each method was believed accurate to about ±1 per cent. The ages listed in Table 1 were calculated, using the following half-lives: U^{238}: $4{\cdot}51 \pm 0{\cdot}01 \times 10^9$ years (Kovarik and Adams, 1941); U^{235}: $7{\cdot}13 \pm 0{\cdot}16 \times 10^8$ years (Fleming, Ghiorso, and Cunningham, 1952); Th^{232}: $13{\cdot}9 \pm 0{\cdot}3 \times 10^9$ years (Kovarik and Adams, 1938). The errors quoted in the ages are entirely analytical and do not include possible errors in half-lives. The presently accepted half-life for U^{235} is $7{\cdot}13 \times 10^8$ years, with a probable error $\pm 0{\cdot}16 \times 10^8$ years. This uncertainty introduces additional errors of ±35 m.y. in the U^{235}-Pb^{207} age and ±90 m.y. in the Pb^{207}-Pb^{206} age of the uraninite, which do not appear in Table 1. At present we prefer not to emphasize the Pb^{207}-Pb^{206} age, because it depends strongly on a possible error in the present value of the half-life of U^{235} as well as on the uncertainty of a correction in the lead ratios for discrimination due to the effect of the magnetic field of the spectrometer on the electron multiplier, which was used in order to permit isotopic analysis of microgram amounts of lead.

The uranium-lead ages are seen to be concordant, while the thorium-lead age of the uraninite is 8·6 per cent lower than the uranium-lead ages of the mineral. This agrees closely with the findings of Wasserburg and Hayden (1955) for five uraninites and may indicate either an error in the value of the half-life of thorium in current use or a uniform pattern of loss of Pb^{208} or gain of Th by uraninite. However, the discrepancy should not be emphasized, since an appreciable normal Pb correction had to be made to the Pb^{208}, necessitating the accurate measurement of an extremely small Pb^{204} peak.

Rubidium-strontium Age Determinations

Age determinations, using the decay of Rb^{87} to Sr^{87}, were made on fresh samples of lepidolite, muscovite, and microcline collected at the same time as the uraninite. In addition, the results of an analysis of another sample of lepidolite which was made several years ago are reported (Sample A). This is the sample discussed previously (Davis and Aldrich, 1953), and the difference in ages arises from the use of a slightly different decay-constant.

These minerals were analysed for Sr^{87} and Rb by isotope dilution, making the chemical separations by an adaptation of ion-exchange techniques described previously (Aldrich, Doak, and Davis, 1953). The decay-constant used for the disintegration of Rb^{87} was $1{\cdot}13 \times 10^{-11}$ yr^{-1}. In all cases the Sr^{87} was greater than 95 per cent radiogenic.

The results of the chemical analyses are shown in Table 4.

Table 4. Rb-Sr analyses and ages

Mineral	Rb (weight per cent)	Radiogenic Sr^{87} (p.p.m. by wt)	Rb-Sr age (m.y.)
Lepidolite			
Sample A	1·19	72·6	1890
Sample B 1	1·08	72·9	2080 ± 100
2	1·10	72·5	2040 ± 100
3	1·15	74·9	2025 ± 100
Muscovite	0·409	28·2	2130 ± 100
Microcline	0·679	43·0	1970 ± 150

The three sets of data for lepidolite sample B show the results of replicate analyses on the same crushed and sieved sample. The difference between the results for sample A and sample B may be attributed to improvements in the techniques of Rb analysis during the the three years which elapsed between these analyses.

It may be noted that the Rb-Sr ages are consistently higher than the U-Pb age of 1600 m.y. This is in agreement with comparisons of Rb-Sr and K-A ages which have been made previously (Wetherill, Aldrich, and Davis, 1954; Aldrich, Davis, Tilton, and Wetherill, 1956) and with comparisons with less reliable U-Pb ages. However, the effect is most clearly shown in this comparison with concordant U-Pb ages on a fresh uraninite sample. The consistency of the differences suggests the possibility that the discrepancy arises from an incorrect decay-constant. A value of $4{\cdot}9 \times 10^{10}$ years for the half-life of Rb^{87} would make the Rb-Sr ages agree with the uraninite ages within experimental error. Geese-Bähnisch and Huster (1954) have recently questioned the accepted value of the decay-constant of Rb^{87}. They have measured the half-life to be $4{\cdot}3^{+0{\cdot}3}_{-0{\cdot}2} \times 10^{10}$ years as compared with the older values of about 6×10^{10} years. Use of this decay-constant instead of the older value will make the Rb-Sr ages less than 1600 m.y.

K-A Age Determinations

K-A ages were determined on the samples of lepidolite, muscovite, and microcline which were collected with the uraninite in 1954 and for which the Rb-Sr ages are reported in the previous section.

Potassium determinations were made by isotope dilution, using K^{41} tracer, and by flame photometry. The results of the two analytical methods agreed within about 5 per cent or better, and the average was used.

Argon determinations were made, using A^{38} tracer prepared by irradiating chlorine in a nuclear reactor. The A^{38} tracer samples were made and calibrated by the method described by Hayden and Inghram (1953), and contained about 10^{-5} cm^3 STP of A^{38}. The tracers used in this work differed from those used by Wasserburg and Hayden (1955) only in that they contained about 10^{-3} cm^3 of Xe. This gas is more readily adsorbed than argon and will tend to saturate the adsorptive capacity of the glass walls and thus prevent adsorption of argon on the walls of the glass break-off tubes.

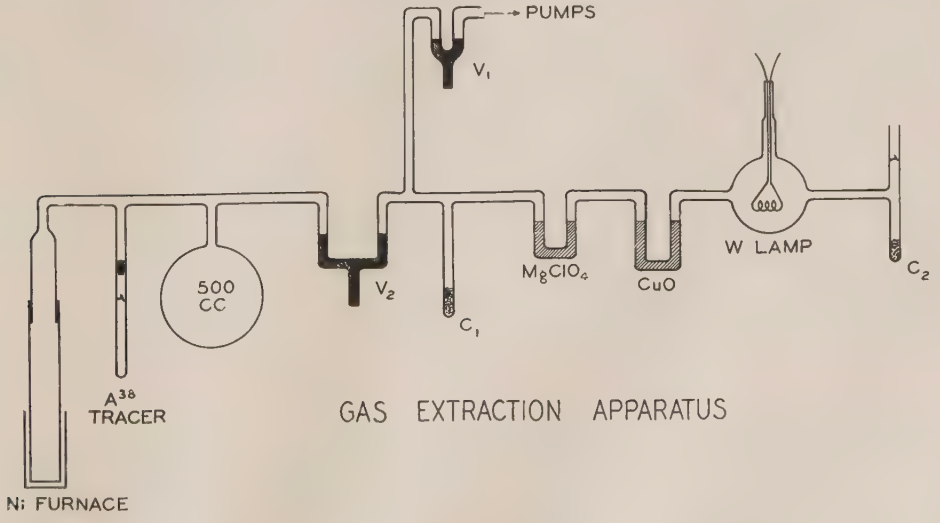

Fig. 1.

The apparatus used to prepare the argon samples is shown in Fig. 1. After the system is pumped down and the charcoal adsorbers and reagents outgassed, the system is isolated from the pumps by raising the mercury cut-offs V_1 and V_2. The A^{38} tracer is admitted by breaking the break-off tip of the tube in which it is enclosed. About 2 g of mineral are then fused in vacuum-melted NaOH in the electrically heated nickel furnace. The reaction is allowed to continue for four hours, after which the mixture of gases is transferred to the charcoal tube C_1 with liquid nitrogen. The cut-off V_1 is then raised and the gas released into the purification train between the charcoals C_1 and C_2. Water is removed by magnesium perchlorate, H_2 and CO by hot copper oxide, and oxygen and hydrocarbons by the incandescent tungsten filament. This leaves nitrogen and CO_2 as the principal impurities. These gases do not interfere with the analysis of argon in the mass spectrometer. The purified sample is collected on charcoal C_2, which is then sealed off. The sample is sealed onto the gas sample system of a 6-in. 60° mass spectrometer, and analysed. The measured A^{40}/A^{38} ratio is of the order of 100. The mass-36 peak is used as an indication of normal argon. The samples analysed for this report were all greater than 99 per cent radiogenic.

The results of the K-A analyses are shown in Table 5.

Table 5. K-A analyses and ages

Mineral	K per cent (wt.)	A p.p.m. (wt.)	A^{40}-K^{40}	K-A age (m.y.)
Lepidolite	8·4 ± 0·3	1·21 ± 0·04	0·118	1500 ± 70
Muscovite	8·5 ± 0·3	1·43 ± 0·05	0·137	1650 ± 80
Microcline	11·2 ± 0·3	1·17 ± 0·04	0·0862	1210 ± 50

The ages were calculated using the disintegration constant $\lambda_{\beta^-} = 5{\cdot}08 \times 10^{-10}$ yr and the branching ratio $\lambda_K/\lambda_{\beta^-} = 0{\cdot}100$. These are the constants recently reported by Suttle and Libby (1955). There is still considerable uncertainty in the true value of these constants, particularly in the branching ratio. Wasserburg and Hayden (1955) have calculated a branching ratio of 0·085 by comparing the K^{40}-A^{40} ratios of feldspars with concordant U-Pb lead ages of uraninites from the same pegmatites. However, the discrepancy between the feldspar and mica ages found in this investigation as well as in previous measurements on other pegmatites and granites (Wetherill, Aldrich, and Davis, 1955) throws considerable doubt on the validity of this value of the branching ratio. Recent counting experiments have led to a higher value of the branching ratio. The value of Suttle and Libby used here is probably as reliable as any available.

It may be seen from Table 5 that the muscovite age is somewhat higher than the uraninite age, the lepidolite age is lower than the uraninite age, while the microcline age is much lower. A possible interpretation of these data is that the true branching ratio is slightly higher, about 0·105, and that the lepidolite has lost a small amount of argon throughout geological time, while the microcline has lost a larger amount. It is too early to give a decisive interpretation of these results, and more information must come from studies of this sort on other geological units and from improved counting experiments.

Conclusions

The results of these measurements fit into the general pattern which is developing from measurements on various geological units. This is that the Rb-Sr ages are too high by a rather consistent factor of about 25 per cent and that K-A ages on micas give fairly reliable ages using a branching ratio of 0·100. Furthermore, the K-A ages of the feldspars

seem uniformly too low. The Rb-Sr ages of the feldspars indicate that they are about the same age as the micas. Thus it seems probable that the feldspars are for some reason more susceptible to loss of argon than are the micas. The very remote possibility that the branching ratio of K^{40} is appreciably different in feldspar and mica has been eliminated by performing counting experiments on these minerals.

The disagreement of these results with those of AHRENS (1949) is probably related to the errors in spectrochemical analyses which have been reported by others (HERZOG, 1955). The discrepancies with the results of TOMLINSON and DAS GUPTA (1953) are more difficult to understand. One possibility is suggested by their statement that they used much smaller samples of rubidium for their mass spectrometric analyses than were used in this work. We have found that when very small rubidium samples are used, the problem of rubidium contamination is serious enough to cause this discrepancy. Their rubidium analyses are invariably higher than those found in this laboratory.

At present, similar investigations are being made on other pegmatites from different localities and of different ages.

Acknowledgements—The authors are indebted to JAMES J. NORTON of the U.S. Geological Survey for help in collecting the samples, and to W. S. MACKENZIE of the Geophysical Laboratory for valuable mineralogical and petrological advice.

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LETTER TO THE EDITORS

Spectres d'absorption infra-rouge de quelques verres naturels entre 2 et 24 microns

(*Received* 19 *February* 1956)

Abstract—The spectra of obsidians and tektites are presented. They are found to be similar to those of industrial glasses.

R. Stair (1955) a publié récemment les spectres d'absorption de quelques tektites dans le visible et l'infra-rouge. L'absorption était complète à partir de 5 microns, malgré l'épaisseur réduite des échantillons. Le méthode des pastilles de KBr, proposée simultanément par M. M. Stimson et U. Schiedt (1952) nous a permis d'obtenir le spectre de 5 tektites et de deux obsidiennes jusqu'à 24 microns. Les spectres ont été enregistrés au moyen d'un spectrographe Perkin Elmer à double faisceau, modèle 21. Les verres naturels étudiés proviennent des endroits suivants:

Tektite I: Konurig, Tchiou-Liou (Chine).

Tektite II: Haï-Nan (Chine).

Tektite III: Dalat (Viet Nam).

Tektite IV: Nord Cambodge.

Tektite V: Pugabadoz (Philippines).

Obsidiennes: de la région volcanique de Cactus Peak, proche du Mojave Desert, California, U.S.A.

Pour les cinq tektites, les spectres obtenus sont très semblables les uns aux autres. Il en est de même pour les spectres des deux obsidiennes. La courbe *a* de la figure représente le spectre de la tektite I; la courbe *b*, celui d'une obsidienne. Ces spectres ressemblent à celui d'un verre industriel, comme le montre la courbe *c*. Les bandes à 8,5 (inflexion), 9,5–12,7 et 21,6 microns peuvent être considérées comme les vibrations fondamentales du tétraèdre SiO_4, cellule de base des corps vitreux dérivés de la silice. Dans le spectre de la tektite I, la bande à 10,6 microns, apparaissant dans le profil de celle à 9,5 microns, révèle la présence d'un oxyde alcalin ou alcalino-terreux intervenant dans une proportion supérieure à 10% dans la composition chimique de la tektite. Le spectre de l'obsidienne est semblable à celui d'un verre contenant un pourcentage très élevé de silice.

L'origine des tektites a fait l'objet de nombreuses controverses. Une mise au point de la question vient d'être publiée par H. C. Urey (1955). L'hypothèse d'une origine lunaire de tels matériaux est actuellement abandonnée au profit d'une origine terrestre. En effet, les tektites ont une composition chimique identique à celle de certains matériaux sédimentaires. Mais a-t-il pu exister sur la Terre, des températures assez élevées pour provoquer la formation de tektites? L'hypothèse d'un réchauffement local de la croûte terrestre lors de l'impact d'un météorite géant a été envisagée. En effet, des couches de tektites d'une épaisseur allant jusqu'à

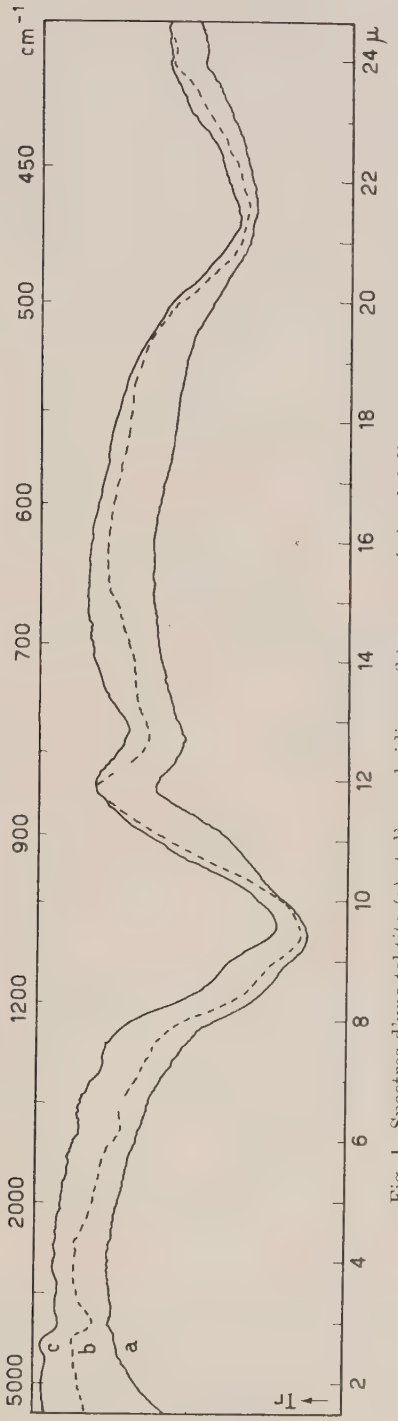

Fig. 1. Spectres d'une tektite (a) et d'une obsidienne (b), comparés à celui d'un verre industriel (c).

15 cm ont été découvertes au fond du Meteor Crater en Arizona. La présence d'un oxyde alcalin ou alcalino-terreux dans la tektite, révélée par le spectre infra-rouge, indique qu'une température de 1200°C à 1400°C est suffisante pour la former.

Nous tenons à exprimer tous nos remerciements à Monsieur le Professeur P. Swings, qui nous a suggéré ce travail et nous a remis les deux obsidiennes, ainsi qu'au R. P. Junkes, Directeur du Laboratoire de Recherches du Vatican, qui nous a transmis les cinq tektites.

Léo Houziaux

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ANNOUNCEMENT

A special double number of *Geochimica et Cosmochimica Acta* (Vol. 10, Nos. 1/2) is to be published in August, 1956.

This issue will contain the following papers:

(1) Dissolution and precipitation of silica at low temperatures by Konrad B. Krauskopf.

(2) Silica in hot-spring waters by Donald E. White, W. W. Brannock, and K. J. Murata.

(3) Potassium-argon dating by R. E. Folinsbee, J. Lipson, and J. H. Reynolds.

(4) Untersuchungen zur Geochemie des Bleis by Karl Hans Wedepohl.

The issue will contain approximately 150 pages.

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6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods. record of experimental results, etc.) for printing in smaller type.

Irradiation
Colours and Luminescence
A Contribution to Mineral Physics

By Dr. Karl Przibram
Emeritus Professor of Physics at the University of Vienna

Translated and revised in collaboration with the author
By John Espenett Caffyn
Lecturer in Physics, Durham Colleges in the University of Durham

In his book *Verfärbung und Lumineszenz*, Professor Przibram provided an extensive treatment of colouration in minerals, and the luminescence which is associated with it. Due to the author's familiarity with the work carried out in Vienna and Göttingen, it was perhaps considered more thoroughly than the work carried out elsewhere, but Professor Przibram omitted no important work in the field, notwithstanding the difficulty experienced in obtaining recent Russian literature.

In the translation, Dr. Caffyn took the opportunity of revising the text, and some 500 additional references were added. Professor Przibram provided new material to make *Irradiation Colours and Luminescence* a completely up-to-date critical survey, and the only recent book which describes the colourations and luminescence produced by exposure to ionizing radiation of both natural and synthetic crystals.

In this book the mineralogist will find how far present-day physical methods will explain some of the phenomena puzzling to mineralogists: the physicist, interested in the solid state, may be assisted to a better understanding of the nature of imperfect crystals.

Ample scope for further studies is provided in the extensive references in the text and the 49 pages of bibliography.

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